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Transport of Oily Pollutants in the Coastal Waters of Lake Michigan; An Application of Rare Earth Tracers

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16. ABSTRACT
A method was developed for tagging oily waste with dysprosium and the associated fresh water with samarium. Neutron activation analysis permitted determination of rare earth concentrations as low as 40 ng/L in 15-mL water samples. Shipboard sampling procedures were developed that allowed measurement of the three-dimensional distribution of the spreading wastes and associated water. The method was applied in two field experiments that involved tracing oily wastes and polluted water from the Indiana Harbor Canal (IHC) into Lake Michigan.

For a summer, floating-plume experiment, about 1400 shipboard samples were collected. Employment of the dual-tracer technique led to the following results: (1) after artificial mixing into the water column by a passing ship, the tagged oil did not immediately resurface, and (2) there were no distinguishable differences between the movement of the oil and water over 4 km of travel.

During a winter, sinking-plume experiment, 1200 lake-water samples were collected from a boat and from the raw-water intakes of Chicago's South Water Filtration Plant (SWFP). These data provided positive evidence of the intake of IHC effluent and oily waste at the SWFP. The different tracers for the oily waste and underlying water gave evidence of separate pathways to the SWFP, reflecting differing transport modes for surface and near-bottom waters.

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An Application of Rare Earth Tracers

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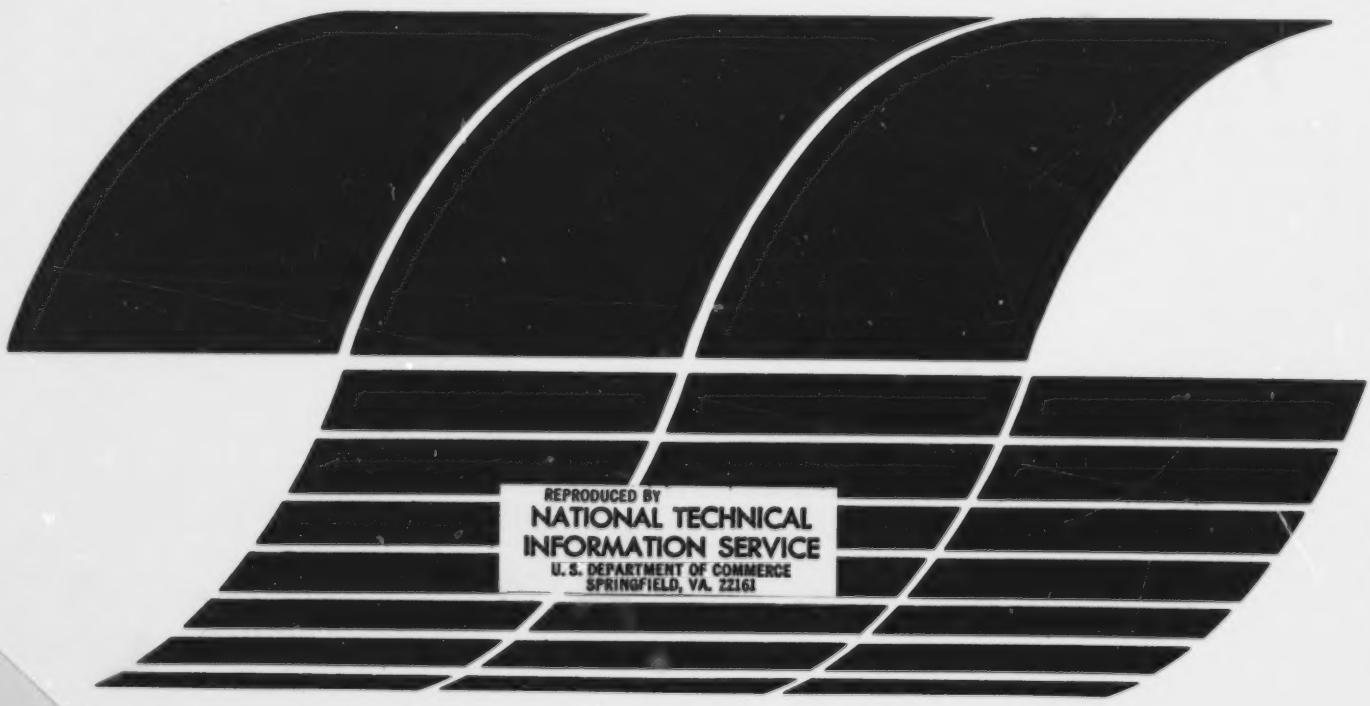

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WATER RESOURCES RESEARCH PROGRAM

TRANSPORT OF OILY POLLUTANTS IN THE COASTAL WATERS OF LAKE MICHIGAN

An Application of Rare Earth Tracers

by

D. L. McCown, K. D. Saunders, J. H. Allender, J. D. Ditmars, and W. Harrison

Energy and Environmental Systems Division
Argonne National Laboratory Argonne, Illinois 60439

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FOREWORD

The U.S. Energy Research and Development Administration (ERDA) was formed in January, 1975. Shortly thereafter, certain energy-related research programs being conducted by the U.S. Environmental Protection Agency (EPA) were transferred to the ERDA's jurisdiction. Funding for the programs was also transferred ("passed through") from EPA to ERDA, giving rise to the designation of such research programs as "pass-through" programs.

One of the EPA-to-ERDA pass-through programs was entitled "Offshore Oil Extraction and Related Problems." A task within this program was entitled "Transport and Dispersion of Refinery Wastes in Freshwater Coastal Regions." This research task was undertaken by Argonne's Energy and Environmental Systems Division (EES).

The original task description called for field experiments using rare earth tracers to tag both a release of oily refinery wastes and the underlying waters in the Indiana Harbor Canal (IHC) that discharges into southwestern Lake Michigan. The IHC discharge forms a thermal plume in the lake because the canal receives copious volumes of steel-mill process water. Also, an oil refinery is situated on the canal, and its effluents, as well as those from other industries and municipal wastewater treatment plants, provide oily wastes to the canal waters. Subtask descriptions originally included an experiment during winter sinking-plume conditions and three experiments during several summer floating-plume conditions. Initial plans also called for the development of a mathematical model, based on experimental data, for prediction of the transport and dispersion of the refinery wastes. The original task duration was to be five years.

Termination of the task after 2 1/2 years duration resulted in a modified scope of work. One sinking-plume experiment and only one floating-plume experiment were completed. The modeling effort proposed originally was not undertaken. An earlier report, "Transport and Dispersion of Oil-Refinery Wastes in the Coastal Water of Southwestern Lake Michigan (Experimental Design--Sinking-Plume Condition)," ANL/WR-76-4, July, 1976, by McCown *et al.* described initial experimental designs and procedures. The present report is a final task report on the results of the application of the tracer techniques in the sinking- and floating-plume experiments.

TRANSPORT OF OILY POLLUTANTS IN THE COASTAL WATERS OF LAKE MICHIGAN: AN APPLICATION OF RARE EARTH TRACERS

by

D. L. McCown, K. D. Saunders, J. H. Allender,
J. D. Ditmars, and W. Harrison

ABSTRACT

An experimental method was developed to tag and to trace oily pollutants in fresh water environments. The use of two rare earth element tags (Dy and Sm) permitted simultaneous tracing of small oil spills at the water surface and of the underlying water. Neutron activation analysis was used to determine the tracer concentrations in numerous, small water samples collected from a moving boat.

The method was applied in two field experiments with simulated oily pollutants in the Indiana Harbor Canal (IHC). Industry draws water from Lake Michigan for cooling, and the water is returned to the Lake via the IHC. When the lake water temperature is > 4°C, the IHC effluent floats out on the surface. When the lake water temperature is < 4°C, the IHC effluent forms a sinking plume. Tagged oily pollutants and IHC waters were traced under both floating- and sinking-plume conditions.

Floating-plume results indicated that oily waste artificially mixed downward by a ship did not resurface, no differences were seen in the movement of the oily waste and the underlying water, and mixing coefficients for tagged oil and water were similar to those measured by others on the Great Lakes.

Sinking-plume results gave unequivocal evidence of the intake of IHC effluent at Chicago's South Water Filtration Plant and indicated partitioning of the oily wastes and water. Simple dilution estimates for the sinking plume were supported by the tracer data and similar estimates indicated plume center-line dilution ratios for the entire IHC effluent at the water intakes could be as low as 2.8.

EXECUTIVE SUMMARY

This report presents the results of research conducted by Argonne National Laboratory for the U.S. EPA and U.S. ERDA. The objectives of the research were to develop a method to tag simultaneously and trace oily wastes and the underlying waters and to apply that method to specific contaminated fresh coastal waters.

The tagging technique utilized rare earth element (REE) tags. Dysprosium (Dy) was chosen to tag the oily waste and samarium (Sm) complexed with a chelating agent (DTPA) was used to tag the underlying water. A three-dimensional, underway sampling system employing electronic boat positioning was developed for the over-water tracking phase of the project. Subsequent tag detection and concentration determinations were by Neutron Activation Analysis (NAA) performed at ANL's CP-5 reactor. The NAA technique developed had the following significant features:

1. Minimum detectabilities of 6×10^{-10}g for Dy and 2×10^{-8}g for Sm were achieved with small water samples (15 mL),
2. The samples were collected and subsequently irradiated in the same polyethelene containers, Polyvials,
3. No pre-irradiation sample preparation except evaporation of the liquid phase and cleaning of the outside of the Polyvial was necessary,
4. The short half-lives of Dy and Sm permitted a rapid rate of analysis (17 samples per hour), and
5. Dy and Sm could be easily detected and quantified at the same time.

The tracing technique was applied to experiments in the Indiana Harbor Canal (IHC) which discharges into Southwestern Lake Michigan about ten miles south of Chicago. The source of IHC water is Lake Michigan. Industry along the canal draws water from the lake and uses it for cooling processes. The water is heated 5-8 C° and dumped back into Lake Michigan via the IHC.

The flow regime in the IHC varies from winter to summer. In the winter, when IHC effluent meets ambient Lake Michigan water (< 4°C), a plume of 4°C (maximum density) water is formed and sinks near the IHC entrance. However, in the summer (when ambient lake water is > 4°C) the canal effluent flows out on the surface and lake water intrudes into the canal along the bottom.

Waters of the IHC are heavily polluted by the industry along the canal. When the plume is sinking and winds are southerly, the City of Chicago's South Water Filtration Plant (SWFP) experiences periods when large amounts of costly charcoal must be used to eliminate the high hydrocarbon

odors from it's lake raw-water supplies (the SWFP's only source of fresh water). These odors have long been theorized to come from IHC water migrating up the coast along the bottom. Thus, a secondary objective of this study was to attempt to provide proof of the transport of IHC water to the SWFP.

Tracing experiments were conducted on two occasions, once for the floating-plume and once for the sinking-plume. On September 24, 1976 the canal was tagged *in situ* with 4.5 kg (10 lb) of Sm complexed with DTPA, and with 3 Kg of rhodamine WT dye. At the same time and location 57 L of oily waste tagged with 0.5 kg (1 lb.) of Dy was poured on the canal surface. Approximately thirty minutes after tagging an empty ore carrier passed directly through the center of the dye patch. During the following ten hours, the plume was mapped four times and about 1200 15-mL water samples were collected. The results indicated that, after the oily waste was artificially mixed into the water column by the passing ship, it did not resurface but remained mixed, no distinguishable differences were seen in the movement of the oily waste and underlying water, and calculated diffusion coefficients for both Sm and Dy were similar to values measured by others on the Great Lakes and were of the order 10 m^2/s.

The sinking-plume experiment was conducted on March 2-4, 1977. The canal was tagged *in situ* on March 2, 1977, with 13.6 kg (30 lb.) of Sm complexed with DTPA, and with 7.5 kg of rhodamine WT dye. At the same time and location 170 L of oily waste tagged with 1.4 kg (3 lb.) of Dy was poured on the surface of the canal. The tagged patch was followed for about 50 hours and about 1000 water samples were collected from a moving boat. During the same time interval, 240 samples were collected from the raw-water streams at the SWFP. The results of the sinking-plume experiment gave unequivocal evidence of the transport of polluted IHC water to the SWFP, indicated a partitioning of the surface oily wastes and the underlying water, and supported simple plume dilution estimates at the SWFP. Furthermore, similar estimates indicated plume center-line dilution ratios for the entire IHC effluent plume could be as low as 2.8.

1 INTRODUCTION

1.1 PURPOSE AND SCOPE OF STUDY

There is at present an inadequate understanding of the processes of transport and dispersion of oily wastes in coastal waters. It was the purpose of the present program:

1. To develop methods for simultaneously tagging both oily wastes and the underlying waters, each with a unique tracer, and for determining their individual motions in fresh coastal waters, and
2. To apply these methods to specific, contaminated coastal waters.

The studies by Argonne National Laboratory (ANL) were devoted to a series of experiments conducted on oily wastes that move into the coastal waters of southwestern Lake Michigan from the Indiana Harbor Canal (Fig. 1.1). Several possible sources of oily pollutants in the canal exist. Effluents from an oil refinery, steel mills, and municipal sewage treatment plants contain such pollutants. Small spills from oil transfer facilities and run-off from industrial sites also contribute to the oily-waste loading. For this study no individual source was tagged, but rather a simulated oily-waste was prepared (see Sec. 2.1.2.2) and spilled in the canal.

The source of water in the canal is Lake Michigan. Industry draws water from the lake, uses the water for industrial cooling processes which heat the water 5-8 C°, then returns the water to the canal. The canal water moves into the lake as a thermal plume, sinking during much of the time in winter, and forming a surface plume during the remainder of the year. Significant differences in the oil-transport regime are expected during floating and sinking-plume conditions. The most difficult transport/dispersion regime to observe in the field is that of the sinking plume, because it is difficult to follow and sample a tagged mass of canal water that forms only a thin layer (commonly 1- to 5-m thick) as it spreads over the bottom. Nevertheless, the importance of sinking-plume transport in carrying contaminants from the Indiana Harbor Canal (IHC) to municipal water intakes in southwestern Lake Michigan dictated devoting significant efforts and resources to the tagging and tracing of IHC water during sinking plume conditions.

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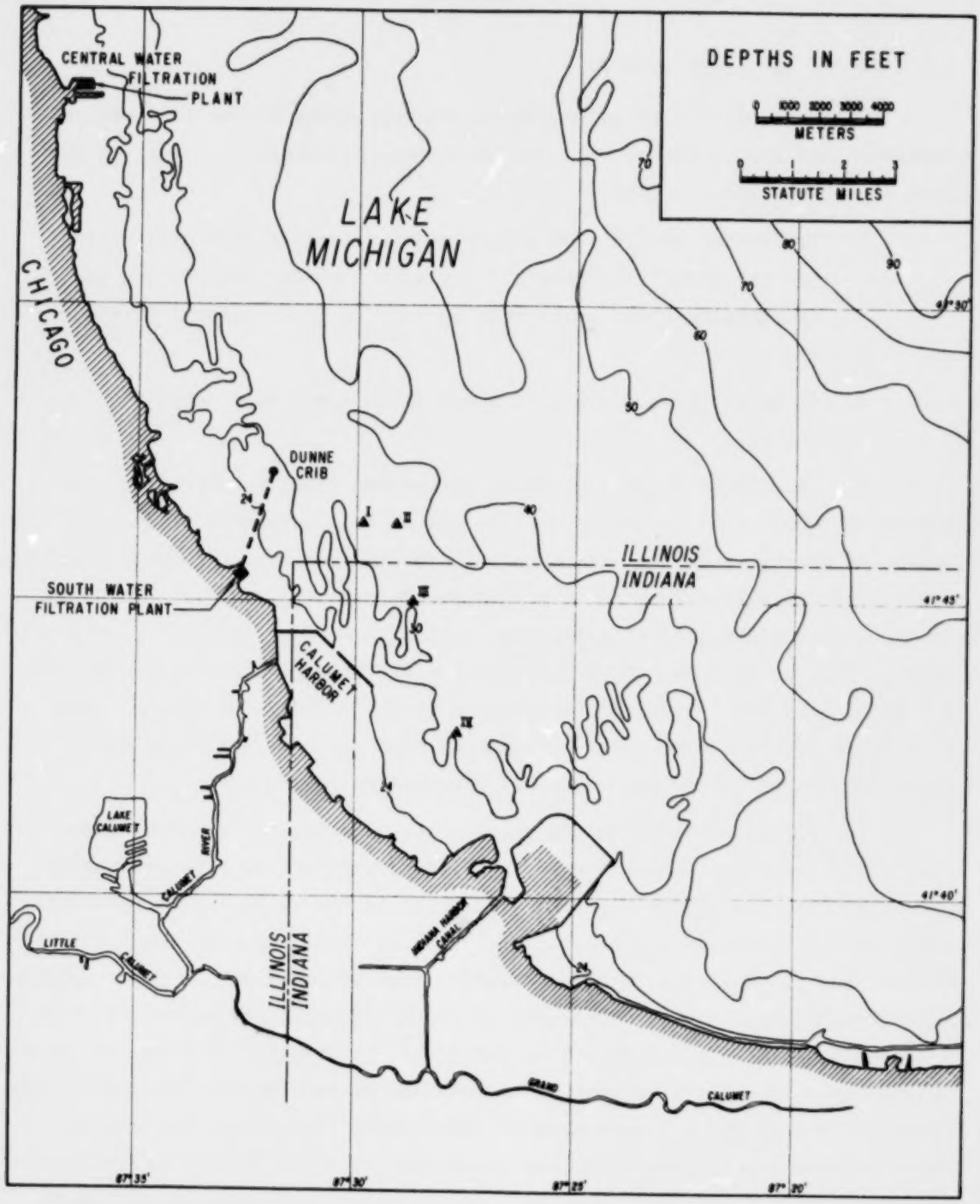

Fig. 1.1. Location Map for Study Area and Current-Meter Positions (I-IV) in Southwestern Lake Michigan

Two major field studies were conducted during the project: a summer floating-plume and a winter sinking-plume study. The results of both studies are given in this report and the methods for tagging with rare earth elements and analyzing water samples by neutron activation techniques are described.

1.2 RESEARCH APPROACH

1.2.1 Experimental Outline

In general, this study involved tagging a portion of IHC water and simultaneously placing tagged simulated oily-wastes on the surface of that portion of IHC water. The tagged oily-waste and water was then followed, from a boat, and sampled numerous times at many depths. During the summer study, the tagged cloud was tracked and sampled for about 10 hrs and for a distance of about 3.5 km from the IHC entrance.

In the winter, the tagged cloud was tracked and sampled for about 54 hrs from a boat and, in addition, samples were collected at the raw-water intakes of the City of Chicago's South Water Filtration Plant (SWFP) about 12 km north of the IHC entrance. (Fig. 1.1) Current meters were placed in the study area (Fig. 1.1), for the winter study, so that appropriate features of the water movement could be determined. The current meter data (current speed and direction) were used to guide the interpretation of the results of the tracer experiment and to develop a simple model for the transport of IHC water northward to the SWFP.

1.2.2 Tagging and Tracing IHC Water and Associated Oily Waste

It is important to distinguish between the dynamics of waste-receiving waters and the motions of the associated oily wastes within and upon these waters. Adequate understanding of these separate but complementary motions is essential for the development of predictive models. Accordingly, a method was developed for the simultaneous tagging and tracing of oil and water. The method allowed detection of tags with concentrations as low as ≈ 40 ng/L. Traditionally, two classes of substances have been used to tag water or pollutants for tracing: fluorescent dyes and radionuclides. Fluorescent dyes have several drawbacks. Some fluorescent dyes bleach in the sunlight. Others that do not bleach may become absorbed onto suspended particles, which then settle out of the water column. Radionuclides have several advantages

for water and contaminant tracing, but have an unacceptably high radiation hazard for all but very short-term studies.

The approach to tracing in the present study uses stable-element tags and neutron activation analysis (NAA). Among the advantages of this method are the following:

1) there is no radiation hazard to the environment,
2) with samples as small as 15 mL detection is possible to $\simeq$ 40 ng/L of stable-element concentration in the tagged water,
3) there appears to be negligible tracer loss to suspended matter and sediments, and
4) the stable-element tags themselves can be chosen to be non-toxic to the environment.

Certain rare-earth elements (REEs), such as dysprosium, samarium, lanthanum, europium, and ytterbium suggested themselves as likely candidates for tags. Among the REEs available, dysprosium (Dy) and samarium (Sm) were chosen as the most suitable for the present study principally because

1) they have high detectability (see Sec. 2.1.1) and short half-lives, and
2) their natural occurrence in Lake Michigan is at concentrations below the limits of detectability provided by the methods used in the present study.

With regard to point 2 note that, prior to tagging, 24 samples of water were taken from the shore and from the crib intakes of the SWFP and analyzed for their natural Dy and Sm content. No Dy or Sm was detected in the 48 samples that were used to determine background concentrations. Minimum detectabilities in 15-ml samples are 6×10^{-10} g for Dy, and 2×10^{-8} g for Sm, using the Argonne method. The availability of a high-flux reactor and of superior radiation-counting equipment at Argonne, and the existence of precision boat-positioning equipment within the Water Resources Research Program at ANL, made it possible to design a relatively sophisticated experiment for studying the transport of polluted IHC water and simulated oily waste to Chicago's water intakes.

1.2.3 Documentation of Lake Currents

No current data were specifically collected for the floating plume study. Data from an ANL current meter deployed for a separate study about

10 km north of the study area in Lake Michigan indicated lake currents of about 0.03 m/s (the order of current meter threshold values) during the period of the study. Moreover, plume motion was limited to a relatively small region in the lake due to the small currents and short duration of the floating plume experiment.

Three current meters were deployed in a close array directly off the SWFP during the initial feasibility study (McCown et al., 1976). Data from these meters revealed unexpected current patterns between the mouth of the Indiana Harbor and the SWFP. Therefore, a more open deployment of four current meters was made along the line of expected plume flow from the mouth of the Indiana Harbor to the Dunne Crib (Fig. 1.1), during the winter 1977 study.

1.3 PREVIOUS WORK

Channell (1971) used a rare-earth element (La) and neutron activation analysis for tagging and tracing estuarine water. To our knowledge, however, the present study is the first to employ rare-earth elements as tracers in fresh coastal waters. Channell's work will be discussed in detail below, particularly in Sec. 2.1.2.1.

The impact of the IHC effluent on Lake Michigan water quality was investigated by Snow (1974). Comprehensive water-quality data for the IHC and adjacent lakes waters and pollution loadings were gathered from existing data bases. A limited field survey (during floating-plume conditions) during this study resulted in additional measurements of water quality parameters and of currents and temperatures. In addition to suggesting relationships between the loadings and water quality in the lake, Snow pointed out the physical mechanisms thought to be important in the transport and mixing of IHC waters into the lake, i.e. the jet-like efflux of the canal and the intrusion of lake waters under the canal surface waters during the summer.

Lake currents just off the IHC in winter occasionally flow northward. There is some evidence (P. A. Reed, 1975, personal communication) that, when conditions are right for developing a sinking plume, plume-borne pollutants may be transported as far north as the City of Chicago's Central Water Filtration Plant (CWFP),* which draws its water from either the Dever Crib, located

*Recently renamed the James W. Jardine Purification Plant.

3.2 km NE of CWFP (Fig. 1.1) or the shore intake. According to Reed, when currents are flowing northward plume water is commonly transported as far as the intake crib for Chicago's South Water Filtration Plant (SWFP) during winter months. During January 1975, for example, the (SWFP) experienced a two-week period of hydrocarbon odors in its raw water. The severity of the odors was greater in the SWFP's raw water from its shore supply than in the raw water from its Dunne crib (Fig. 1.1). The hydrocarbon odors were accompanied by elevated concentrations of ammonia-nitrogen, and there can be little doubt that a significant percentage of the hydrocarbon odors originated from waters of the IHC. According to permit data (Snow, 1974, v. 1, p. 200), for example, the ARCO refinery, Inland Steel, Youngstown Sheet and Tube, and others are permitted to contribute up to 22,680 kg/day (50,000 lb/day) of oil and grease to the IHC. If the lake temperature is appropriate (less than about 2°C), development of highly polluted sinking plume that is transported northward occurs when

a) there is a significant rainfall in the area (0.64 cm [0.25 in] of rain in a day will cause overflowing of some combined sewers that enter the IHC), and

b) there are brisk winds from southerly quadrants.

Modern studies of currents off Chicago began with two surveys by the U.S. Public Health Service (1963a, 1963b). The first of these used Geodyne Savonius-rotor current meters at three stations off the coast of Chicago. Two of these stations provided current information for the period December 18, 1962 - March 22, 1963. Of these two stations, only station 3 (42°01.7' N, 87°31' W) was near enough to shore (9 km) to be considered useful for coastal current delineation. The prevailing direction of the currents for January 31 - March 22, 1963, was about 150°, with a minor peak at about 340°. The third station (41°50.2' N, 87°29.7' W) was in operation for 6 days during March 1963. These data are interesting and important as they represent the first long-term time series of current measurements in Lake Michigan in the winter. They are, however, not particularly useful in the context of this study, as the current meters were located too far lakeward to resolve the nearshore currents and too far north to be representative of the currents near the Indiana Harbor-Calumet Harbor region.

The second study by the U.S. Public Health Service (1963b) used drogues to measure lake currents in the nearshore zone. This study took place on

April 11-12, 1963, and was of too short a duration to make any available estimates of nearshore currents.

Saylor (1966) reported on the current patterns in Calumet Harbor under various wind conditions. The current patterns were determined from a combination of current meter, drogue and dye measurements. He found that, under southerly winds, the currents from the south did not penetrate into the harbor and were deflected around the end of the breakwater (Fig. 1.1). There was little flow through the opening in the breakwater under these conditions. During periods of northerly winds, a significant current is seen through the breakwater opening with little flow around the end of the breakwater into Calumet Harbor. He concluded that currents due to seiche modes were relatively weak, but important for the flushing of stagnant water in the upper reaches of the harbor.

The next study of currents in the southwestern region of Lake Michigan was performed by D. Frye and L. S. Van Loon of Argonne National Laboratory (Snow, 1974, pp. 117-126). Three Braincon 381 histogram-recording Savonius-rotor current meters were deployed, one adjacent to the 68th St. Crib at a depth of 5.2 m and the other two off the Inland Steel landfill at depths of 3 and 6 m. The currents were measured from November 8 to December 8, 1973. The investigators found a cyclical variation of current speed with the speed minima corresponding to shifts in the current direction. The current directions were generally shore-parallel, and the currents at the crib and off the landfill were similar in direction. This study produced the first moderately long time series of current velocities in the Indiana Harbor-Calumet Harbor region under a period of low stratification, but it suffered from the twofold drawbacks of limited time and the use of Savonius-rotor current meters in shallow water, where waves may bias the recorded velocities.

Monahan and Pilgrim (1975) made current-meter measurements off Chicago from July to October 1974. They found generally northward-flowing currents during this period. This study was inadequate for assessing currents in the Calumet Region, as the stations were located too far north and east (42°00' N, 87°30.0' W and 41°55.5' W), the current meters used were Savonius-rotor meters, and the lengths of the time series were too short.

Saunders and Van Loon (1976) obtained current measurement for June-December 1975, using ducted-impeller current meters. The current meters were

located at mid-depth about 3 km SE of the Dunne Crib. Although the time series was long and the current meters did not suffer from wave-enhanced speeds, the data are still unsuitable for the present study, as most were obtained under periods of strong stratification. Such data cannot be extrapolated to winter conditions when the lake is well mixed.

Although the above measurements give some insight into lake currents in the area of interest, they do not reflect conditions occurring at the time of sinking-plume activity. For this reason, the special measurements described in Sec. 2.3.2 were made.

2 EXPERIMENTAL PROCEDURES

2.1 PLUME-TRACING METHODOLOGY

2.1.1 Tagging Agents

Dysprosium (Dy) was the agent chosen to tag the simulated oily waste, and samarium (Sm) was selected to tag the IHC water. (The neutron-activation characteristics of Dy and Sm are shown in Table 2.1.)

A third agent, the fluorescent dye rhodamine-WT, was used to tag the canal water so that, by means of a pump and fluorometer, the tagged water mass could be detected immediately and followed by the sampling boat.

2.1.2 Tagging Considerations

2.1.2.1 IHC Water Tag (Sm)

Waters of the IHC are turbid and highly polluted. Introduction of a REE tag into the IHC water column in the ionic form would hazard removal of the REE from solution by the formation of insoluble compounds by reaction

Table 2.1. Neutron-Activation Characteristics of Dysprosium and Samarium (from Lederer, 1967)

Reaction	$^{164}Dy\ (n,\gamma)\ ^{165m}Dy$	$^{154}Sm\ (n,\gamma)\ ^{155}Sm$
Half-life ($T_{1/2}$)	75 s	22.5 min
Thermal neutron-capture cross section (σ)	2000 barns[a]	5 barns
Isotopic abundance	28%	23%
Major gamma energy[b]	0.1082 MeV	0.1043 MeV
Minimum detectability per 15 mL sample as determined by experiment	6×10^{-10} g[c]	2×10^{-8} g[c]

[a] barn = 10^{-24} cm^2

[b] From Bowman and Macurdo, 1974

[c] Irradiation time: 90 s; delay to count: 30 s; count: 90 s.

with some of the many species in solution in the IHC or on the bottom of the canal, and removal from solution by adsorption on suspended solids.

Channell (1971) showed that the persistence of lanthanum in waters that are in contact with bottom sediment is almost twice that for lanthanum complexed with EDTA* than for lanthanum dissolved in acid. Channell suggested that chelation would be advantageous for an injection into an area where suspended solids were flocculating or where the water depth would allow significant contact of the tagged water mass with bottom sediments. IHC waters contain an abundance of suspended solids, and, in a sinking plume, this water remains in contact with bottom sediments. Chelation of REE tags, by complexing with DTPA,** was therefore considered necessary.

2.1.2.2 Oily-Waste Tag (Dy)

Numerous bench tests were conducted to determine how well the simulated oily waste retained the Dy tag. The simulated waste was made up from equal parts of 30-W motor oil, #2 diesel fuel, and engine drain oil. The results of the bench testing are discussed in detail, in the Argonne National Laboratory Report ANL/WR-76-4 (McCown, Harrison, and Orvosh, 1976). In summary, the tests showed that ≃ 0.5% of the Dy migrated from the oil into the water over a five-day time span.

Recently, a new series of bench tests were conducted. In these tests, the 1 L of water underlying the surface slick of 1 mL simulated waste was sampled every two days for 12 days by inserting an automatic pipette to mid-depth. Every second day, immediately after sampling, the underlying water was pumped out of the beaker (leaving ~10 mL) and fresh water was poured into the beaker. After 12 days, the water samples were dryed then analyzed by NAA to determine their Dy content. A very small amount (≃1 μL) of the oil was skimmed off the surface of the water after the last water sample was drawn. These oil samples were irradiated to determine if they contained Dy. All of the oil samples were far too radioactive from irridiated Dy to count and quantify but they clearly indicate that a substantial amount of the Dy remained in the oil.

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*Ethylenediaminetretraacetic acid

**Diethylenetriamine-pentaacetic acid (DTPA was chosen because it is cheaper and easier to complex with Sm than EDTA).

The simulated waste of one of the three beakers was a 1-mL portion of the actual tracer used for the floating plume experiment (Sec. 3.1) and was about 1 year old. The percent of Dy that was detected in the water samples from that beaker are shown by the lower curve in Fig. 2.1. The upper curves show the results from beakers in which the simulated oily waste was mixed just prior (≈1 hr) to the beginning of the tests.

The bench tests discussed in ANL/WR-76-4 indicate that, for environmentally reasonable conditions (very thin surface film), ≈0.5% (5×10^{-1}%/mL oil/mL water) of the Dy in the 1 mL of oily waste on the water in the beaker migrated into the underlying 1 L of water. In the new tests the underlying 1 L of water was changed every two days and these tests showed that, on the average, ≈0.4%* of the Dy in the simulated waste/1 mL of simulated waste/1 L of underlying water migrated from the oil to the water. Thus, a Dy "loss factor" (4×10^{-1}% Dy lost/mL oil/mL water) derived in these experiments was used, although different proportions of oil and water may result in different values.

There are two issues that should be noted regarding the bench tests. First, we share the reservations of most researchers concerning the ability to represent natural phenomena in a beaker; however, no better means to determine the retention of Dy by the simulated waste could be found.

Second, the Dy detected in the water could have been carried into the water in small amounts of dissolved or suspended oil rather than actually passing out of the oil solution. The resolution of this final issue is a difficult problem which would require not only the detection of both the Dy and oil in the drawn sample but also a determination whether or not the Dy is dissolved in the oil. We know of no means to do this.

In summary, the bench testing indicates that Dy is a quite acceptable tagging agent for oily type substances.

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*0.4% Dy lost/mL oil/mL water is the average of the 10 points on the upper two curves on Fig. 2.1. (Note, the samples corresponding to two days for the upper curves could not be quantified because they were 10-mL samples and were too radioactive to count. This does not imply that the Dy concentration was much greater; it means that the volumes were too large. Subsequent samples were 5-mL each.)

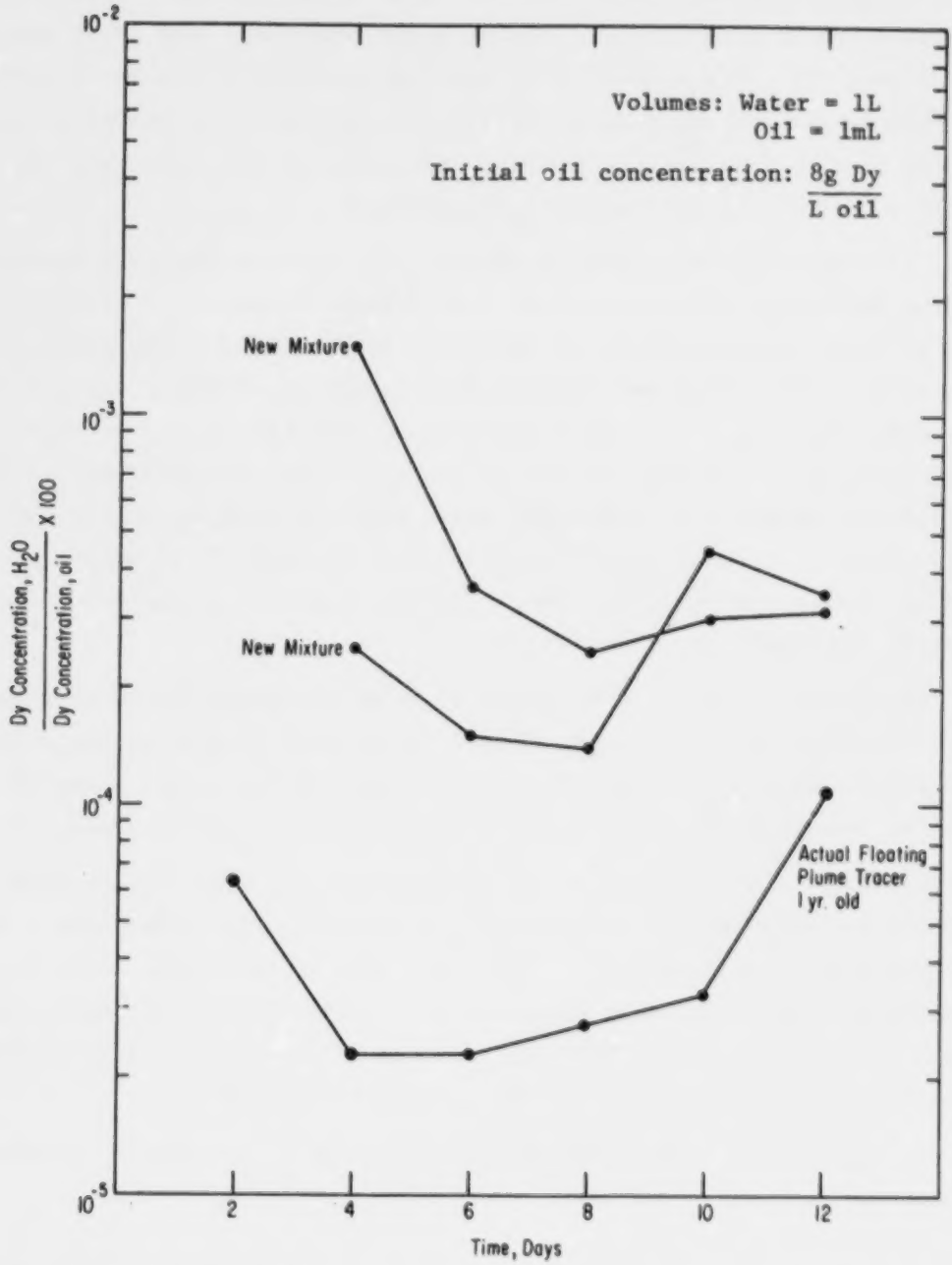


Fig. 2.1. Percent of Dy in Oil Transferred into Water as a Function of the Exchange of Underlying Water (Water Changed Every Two Days)

2.1.3 Sampling Procedures

2.1.3.1 Boat Samples

Documentation of transport and dispersion in a plume requires many data points. This requirement dictates the removal of water samples from several depths and at many locations in the lake. In addition, it is of great importance to know to a high degree of accuracy the position of the boat when samples are being taken. Clearly, electronic boat-positioning equipment and an underway sampling system are required if the area of interest is to be sampled in a reasonable period of time.

Argonne National Laboratory (ANL) has developed a towed-depressor/thermistor array (Frigo, Paddock, and McCown, 1975), and the knowledge gained from ANL's research and development efforts was used to design a three-dimensional water-sampling system. The sampling system includes:

1) a Motorola Mini-Ranger electronic positioning system interfaced with an x-y plotter for real-time positioning,
2) a fluorometer, pump, and hoses to follow the dye patch, and
3) a dynamically depressed faired cable with small tubes attached which extend to the depths to be sampled.

During tracking of a sinking plume an additional large tube is placed in the faired cable to draw bottom water samples. Schematics of the sampling system, as set up for a sinking plume, are shown in Figs. 2.2 and 2.3.

The intermediate-depth water samples are pumped onboard, through 6.4 mm (0.25-in.)-O.D. [4.7-mm I.D.] nylon tubes, by a Masterflex multichannel tubing pump. The flow rate, through ≈20 m of tube, is ≈100 mL/min. This relatively low flow rate was sufficient because each sample was only 15 mL in volume. The tubes are all the same length, so that sample-removal delay times are all equal. The major retarding force in the tube is not hydrostatic head, but friction with the tube sidewalls.

The bottom water sample, collected in the sinking-plume study, is drawn through a 9.6-mm I.D. nylon tube (Fig. 2.3), which is connected to the faired cable at a point 1 m above the depressor fin (Fig. 2.2). The end of the bottom-sampler tube is connected to a 7.3 kg (16 lb) shot that trails the depressor fin by ≈12 m so that the shot is dragging on the bottom. The bottom sampler has a relatively high flow rate, 7.5 L/min and it is driven by a

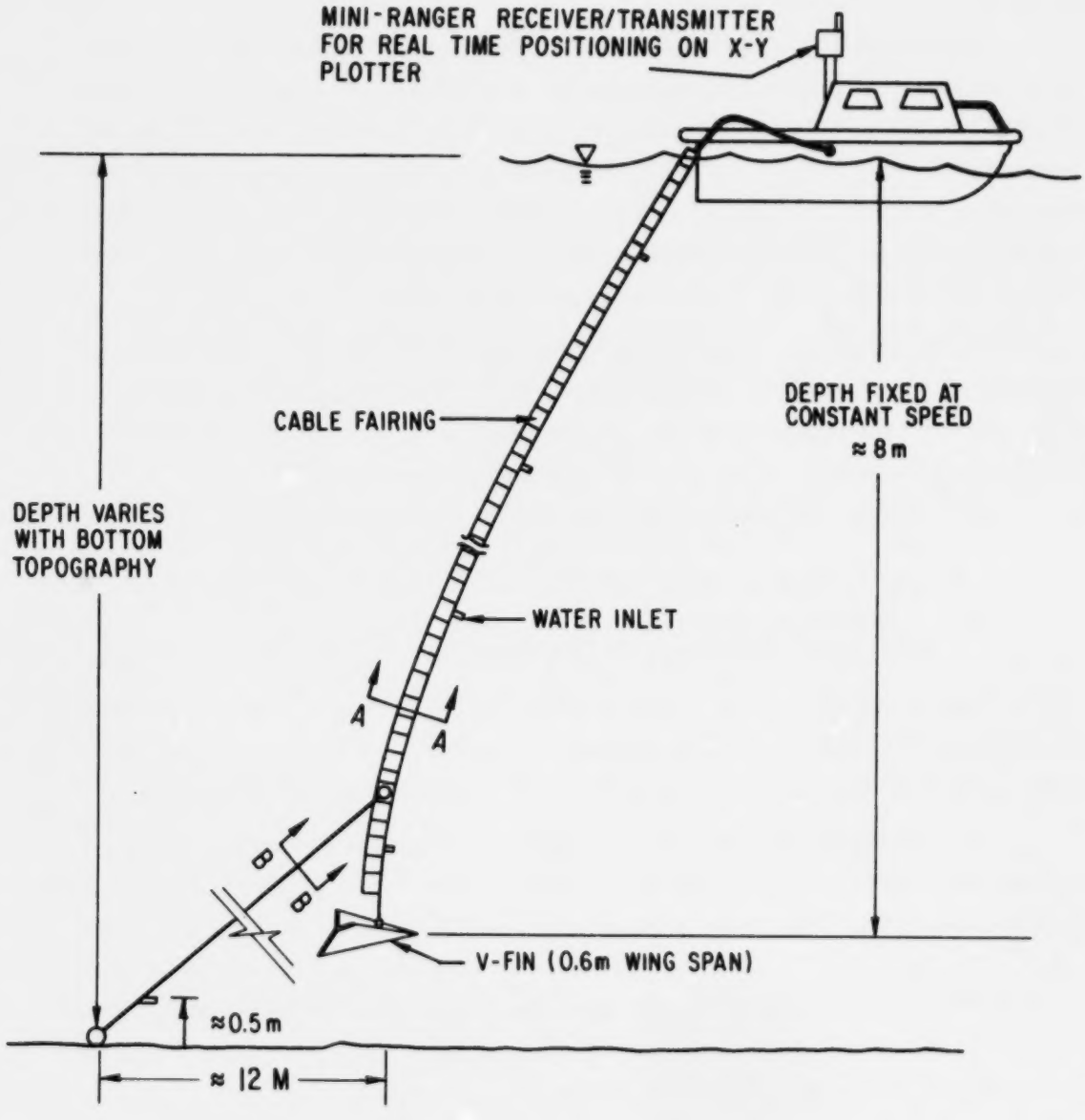
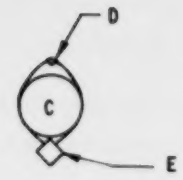
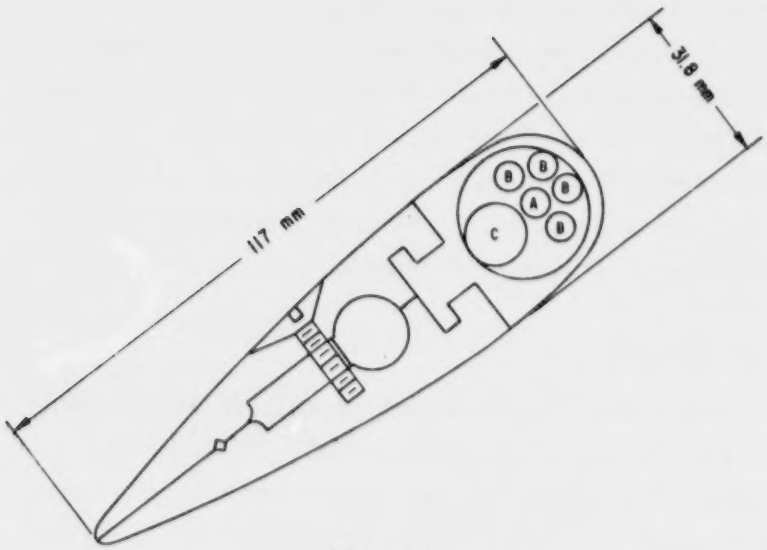


Fig. 2.2. Schematic of the Three-Dimensional Underway Water-Sampling System as Set Up for a Sinking Plume



SECTION B-B



SECTION A-A

A - 6.4 mm (1/4") STEEL CABLE

B - 6.4 mm (1/4") HOLLOW NYLON TUBE

C - 13 mm (1/2") HOLLOW NYLON TUBE

D - 1.6 mm (1/16") STEEL CABLE

E - PLASTIC ELECTRIC CABLE TIE

Fig. 2.3. Cross-Sectional View of the Sampling Chains in Fig. 2.2.

positive-displacement 12-V DC "puppy" pump. Water from the bottom is fed directly to the fluorometer; however, a valved-tee (Fig. 2.4) at the fluorometer inlet diverts a small portion (≈200 mL/min) of the water to the sampling manifold (Fig. 2.4) to be withdrawn for subsequent NAA at Argonne. All the samples for NAA were drawn in new, 15-mL Polyvials.

The bottom sampler was not used for the floating plume study. For the floating plume study, the flow to the fluorometer was independent of the sampling chain and was drawn through a pipe attached to the boat with the intake extending 0.5 m below the water surface. The fluorometer sampler pipe was driven by a 12-V DC "puppy" pump and had a flow rate of ≈20 L/min. After passing through the fluorometer, the flow was exhausted over the stern of the boat.

In addition to the sampling equipment described above, a surface-skimming water sampler was built; however, no acceptable means could be determined to calibrate the surface-skimmer. Samples drawn by the surface-skimmer were collected in the field for both the floating and sinking plume, but the results of the samples collected by the skimmer are presented in only one instance, Fig. 3.6. The surface-skimmer results are not quantitative and can only be an indication of tracer presence or absence.

2.1.3.2 Water-Intake Samples

During the sinking-plume study, water samples were drawn at the SWFP from the raw-water streams for the shore and crib intakes. These 15-mL samples were drawn every 10 min for almost all the period between 2200 hr on March 3, to 1240 hr on March 4, 1977. From 1240 hr to 1600 hr CST March 4, 1977, samples were drawn every 20 minutes. (See Table 2.2 for precise sampling schedule.) Water-intake samples were drawn in the same type of new, 15-mL Polyvials that were used for the shipboard samples. No water samples were drawn at the SWFP for the floating-plume study.

2.1.4 Analytical Procedures

2.1.4.1 Sample Preparation, Irradiation, and Counting

Lake water in the Polyvial samples was evaporated by placing three trays of ≈104 Polyvials each into an oven, set at 80°C, for about 48 hours.

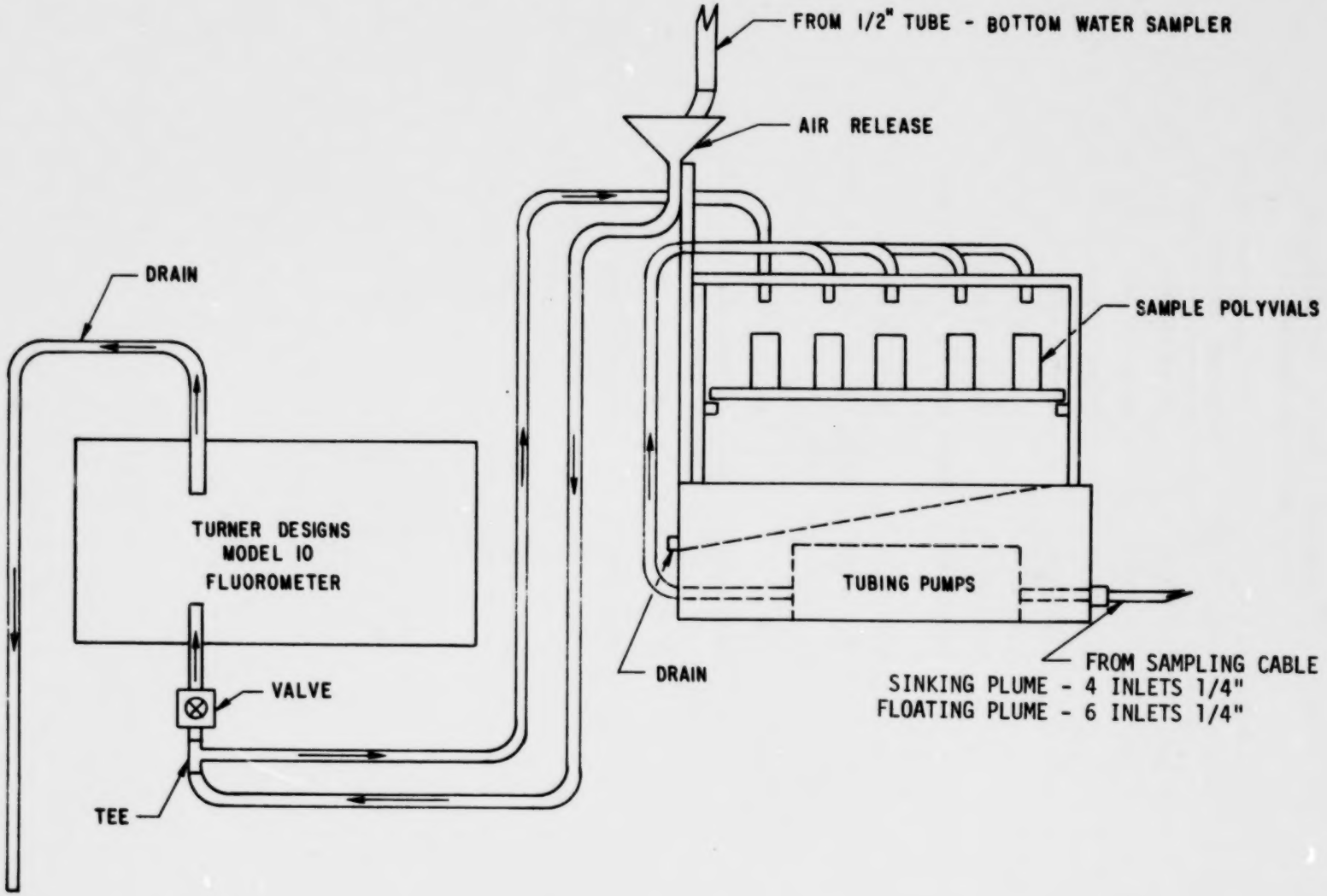


Fig. 2.4. Schematic of Onboard Sampling Manifold and Fluorometer (Bottom-Water Sampler Not Used For Floating-Plume Study)

Table 2.2. Sampling Times at SWFP Crib and Shore Raw-Water Intakes, 1977

Date	Time, hr CST	Sampling Interval
3 Mar.	2200-2350	Every 10 min
4 Mar.	0000-0220	Every 10 min
"	0230-0330	Every 10 min
"	0340-0420	Every 10 min
"	0430-0520	Every 10 min
"	0530-0620	Every 10 min
"	0630-0730	Every 10 min, except @0650
"	0740-0750	Every 10 min
"	0810-0900	Every 10 min, except @ 0830 & 0850
"	0910	Every 10 min
"	0930-1030	Every 10 min, except @ 0940, 0950, & 1000
"	1040-1130	Every 10 min
"	1140-1230	Every 10 min, except @ 1230
"	1240-1600	Every 20 min

Evaporation of the water eliminates ^{19}O gamma-ray interference, the necessity of sealing of the Polyvial before insertion into the reactor, and sample expansion or hydrolysis during irradiation.

Immediately before irradiation, the outside of each Polyvial was washed several times with alcohol to remove NaCl or other surface contamination. The polyvial was then filled with helium, packed into the "rabbit" capsule for insertion into the reactor, and irradiated for 90 s* (timed by stopwatch) in a flux of 2.5×10^{13} n/(cm^2 s^{-1}). During the 30 s that elapsed between the end of irradiation and the start of counting, two steps were performed: (1) the rabbit capsule was removed from the rabbit tube and taken to a hood where the polyvial was extracted, and (2) the polyvial was placed in a sample holder for counting. All samples were counted for 90 s,* and counting started 120 s after insertion of the sample into the reactor flux.

Making the time interval for irradiation, delay, and counting the same for all samples permitted direct comparison of peak areas of particular gammas with the peak areas of calibration samples. This simplified quantification of the amount of Sm and/or Dy in the lake-water samples. Because the time intervals were of equal duration, the ratio of the number of counts (Nc) in a calibration sample's peak to the amount of element (Wc) contained was equal to the ratio of the number of counts in the unknown peak (Nu) to the amount of unknown element (Wu) contained in the sample

$$\frac{Nc}{Wc} = \frac{Nu}{Wu} \text{ , or } Wu = \frac{NuWc}{Nc} .$$

(When time intervals are not equal, the radioactive delay must be accounted for with an exponential decay term and the calculation becomes more difficult.)

The irradiated samples were counted with an Ortec, solid-state lithium-drifted germamium [Ge(li)], low-energy, photon spectrometer (LEPS) with an energy dispersion of 120 eV/channel and a resolution of approximately 250 eV. This detector (Model #8013-25400) had an active surface area of 500 mm^2. The signal from the detector was fed into a Canberra (Model #1468) live-time corrector and then to an Ortec (Model #452) spectroscopy amplifier for pulse

*A few samples taken in Transects C-F (Sec. 3.1.2) of the floating-plume study were irradiated and counted for 120 or 180 s but these samples were quantified by comparing them to calibration samples that were irradiated and counted for the same time as the water samples.

shaping. Finally, the signal went to a Nuclear Data (Model #560), 4096-channel, multichannel analyzer that had a CRT display and a teletype for hard copy. The CRT display had two line markers that could be moved independently through the spectrum for bracketing any particular area of interest.

A hard-copy output could be extracted in two modes. The first mode was a totalizing function that averaged the number of counts in the two channels designated by the markers, then subtracted that average from each channel between the markers. The hard copy in this first mode gave a total number of counts between the markers and a net number of counts. The second mode of output was a channel-by-channel printout of the number of counts in each channel between the markers.

The data were extracted by totaling three equal areas: one area on each side of the peak for background, and the area containing the Sm or Dy peak. The net number of counts due to the peak was calculated by

$$N = T - (2/3)B_N - (1/3)B_F,$$

where

N = net number of counts in the peak,

T = total number of counts in the peak region* (Fig. 2.5),

B_N = total number of counts in the near background (Fig. 2.5),

and

B_F = total number of counts in the far background (Fig. 2.5).

The above-described method of using the total counts and not the net counts to sum the counts under the Sm or Dy peak was superior to using the machine's net calculation. For small peaks, the error, when using the machine calculation, could be quite large because only two channels are used to determine background. When peaks are larger, there is no significant difference between the two methods of determining net counts so, for convenience, the machine's net calculation was used for large peaks.

The NAA procedure allowed analysis of about 17 samples per hour because it was possible to irradiate one sample while the previous one was still being counted.

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*Total number of counts in any region (peak or background) is the number of counts in the first channel, plus the number of counts in the second channel,....., plus the number of counts in the last channel.

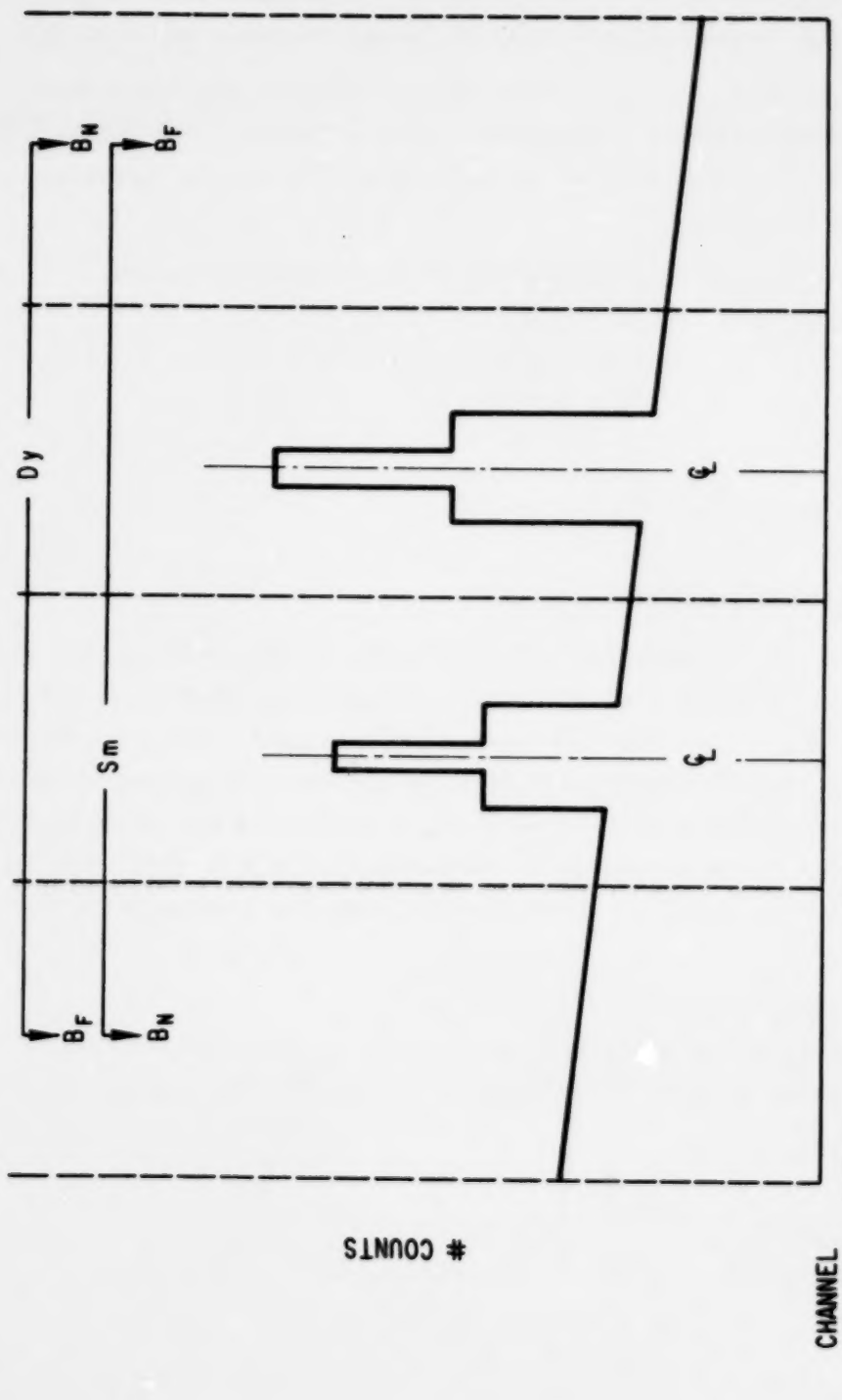

Fig. 2.5. Schematic of CRT Display from Multichannel Analyzer Indicating the Locations of the Sm and Dy Peaks and the Regions Used to Determine Background

2.1.4.2 Error Analysis

Flux variation. The neutron flux in Argonne's CP-5 reactor was controlled automatically to vary no more than $\pm 0.5\%$. Repeated irradiations of a single calibration sample indicated that the actual variance was $< \pm 0.5\%$.

Sample-volume variation. Ten water samples taken in the field were selected at random and weighed to determine volume variation. The volume variation error (1 σ) was found to be <3% by weight. The weight variation of empty polyvials was <0.3%.

Counting statistics. The statistical counting error is generally accepted as

$$e = \sqrt{N} = \sigma$$

with

e = error,

N = number of counts,

and

σ = one standard deviation.

This error reflects the Poisson distribution related to the random nature of radioactive decay. For a detailed analysis, the reader is referred to Livesey's textbook (1966, p. 146-149). The summation of counts under a peak is subject to two statistical errors. The first is the error in determination of the total number of counts in the peak (T). The second error is in the determination of the number of counts in the background $[B = (2/3)B_N + (1/3)B_F]$ that must be subtracted from T to obtain the net number of counts (N) in the peak. That is,

$$N = T - (2/3)B_N - (1/3)B_F.$$

The error in N is due to the error in T, denoted by ε_T, and the error in determining B, denoted by $\varepsilon_B = \sqrt{[(2/3)\varepsilon_N]^2 + [(1/3)\varepsilon_F]^2}$. The percent total error in N, e_N, is

$$e_N = \frac{\sqrt{(\varepsilon_T)^2 + (\varepsilon_B)^2}}{N} \times 100 = \frac{\sqrt{(\varepsilon_T)^2 + (1/9)\ (4\varepsilon_N^2 + \varepsilon^2{}_F)}}{N} \times 100.$$

The statistical error increases with decreasing elemental concentration (lower peaks) and, generally, only becomes a significant factor, considering other errors, when elemental concentrations are approaching the minimum detectable amounts.

Counting geometry. The geometric counting error can be the largest error in activation analysis and one of the most difficult to quantify. This error occurs because the REE, upon drying, becomes distributed in places other than the center of the bottom of the Polyvial. The geometric error was measured by making a number of 1-mL calibration samples with precisely the same amount of Sm. Then some of the calibration samples were filled with distilled water, capped, and shaken by hand. The 1-mL and the full samples (≈ 15 mL) were dried in the oven, irradiated, and counted to determine if a significant difference in the number of counts could be detected. The results for 24 low-concentration full samples were:

$$\text{mean} = \bar{\mu}_F = 397 \text{ counts}$$

$$1\sigma = 32.2 \text{ counts}$$

$$\frac{\sigma}{\mu_F} \times 100 = 8.1\%$$

and the results for ten 1-mL (same concentration) samples were:

$$\text{mean} = \bar{\mu}_1 = 426 \text{ counts}$$

$$1\sigma = 21.5 \text{ counts}$$

$$\frac{\sigma}{\mu_1} \times 100 = 5.0\%.$$

But the statistical error for a typical 1-mL sample that had 429 counts ($\approx\bar{\mu}_1$) was 6.0%, and the statistical error for a full sample with 395 counts ($\approx\bar{\mu}_F$) was 6.5%. Consequently, for these samples, with amounts of Sm approaching the minimum detectable number of counts (100 cts), the geometric variability is of the same order as the statistical error. To be conservative, we will add 7.3% (% difference of $\bar{\mu}_F$ and $\bar{\mu}_1$) to the counts of each sample.

Sampling procedures. Undoubtedly, errors are associated with the sampling procedure; however, no way is known of putting a numerical value on these errors. The method of tagging in no way ensures a homogeneous mixture, although with time the mixture should become more homogeneous, so that samples taken in close proximity can differ markedly from each other and not be indicative of the average concentration in the general area. This type of error is inherent in any type of tracing experiment and is usually neglected,

not because it does not exist, but because it generally cannot be quantified.

Error summary. Of the six types of errors discussed above, three are relatively minor, one is basically undetermined, one increases with decreasing tracer concentration, and one (the geometric error) is treated as constant. For the purpose of reporting results, the errors due to calibration solution, sample volume, and flux variation will be considered insignificant compared to the other errors, and results will be reported as follows:

> sample weight (g) + 7.3% (from geometry) ± statistical counting error (e_N).

Normally, there would also be some error due to the preparation and counting statistics of the calibration sample; however, we have mixed, irradiated, and counted hundreds of calibration samples, and constructed a calibration curve so that these errors are insignificant.

2.2 ANCILLARY ENVIRONMENTAL DATA ACQUISITION

2.2.1 Meteorological Data

Wind data were of primary interest to this study for comparisons with measured currents and pollution events at the SWFP. The closest National Weather Service reporting meteorological station to the study area was at Midway Airport, Chicago. Wind data were generally obtained from the Midway Airport records because the quality of the wind data was slightly better than that which could be obtained at the SWFP and the Midway wind data were available in magnetic-tape format.*

2.2.2 Lake Currents

Because of the short duration (≃ 10 hr) of the floating-plume study, detailed current meter data were not deemed necessary. However, ANL current meters were deployed offshore of the Calumet area for a different study and these data were available to determine the general offshore currents during the floating-plume study. For the sinking-plume study, lake-current data

*We have not made an intercomparison of Midway and SWFP wind data as this would be a study in itself. For the lake-circulation scale of interest, the driving winds are of sufficient speed to be of essentially the same direction at both Midway Airport and the SWFP.

were gathered at the four stations (I-IV) shown on Fig. 1.1. A Bendix Q-15R current-meter sensor was positioned 1.5 m above the bottom at each station; at Station I, a second meter was positioned 5 m above the bottom in order to obtain information on the vertical structure of the currents.

3 RESULTS AND DISCUSSION--FLOATING PLUME

3.1 SUMMER, FLOATING-PLUME RESULTS, SEPTEMBER 24, 1976

3.1.1 Tagging Operation, September 24, 1976

IHC water was tagged *in situ* with 4.5 kg (10 lb) of samarium that had been complexed with DTPA, and with 3 kg of rhodamine WT dye. Volumes released were 38 L (10 gal) of samarium/DPTA solution and 15 L (4 gal) of rhodamine WT solution, respectively. The Sm/DPTA/Rh-WT tag was dispersed in IHC water by pumping the tag through a pipe with small holes drilled along one side. The pipe was lowered over the rail of the boat, and the solution was pumped into the pipe and dispersed at various depths between the surface and -1.0 m through the holes in the pipe. The dispersion process required 20 min and occurred at the location in the canal indicated by the "X" on Fig. 3.1.

The Dy-tagged, simulated oily waste was poured on the surface of the IHC effluent at the same time and in the same location that the *in situ* water tag (Sm) was injected. The oily-waste and tracer consisted of 57 L of the waste mixed with 0.5 kg (1 lb) of Dy. The Dy had been dissolved in a 50% acetic acid solution. Approximately thirty minutes after the end of the tagging operation and before sampling had started, an empty ore carrier passed directly through the center of the dye patch.

The flow in the IHC during the floating-plume study was two-layer. Cool Lake Michigan water flows into the canal along the bottom while warmer IHC water flows out the canal on the surface. Near the canal mouth, where the tagging occurred, each layer is ≈5 m thick. The physical situation in the canal is somewhat analogous to a salt wedge in an estuary and is discussed in detail in Ippen, A. T., 1966.

On the day of the study, September 24, 1976, winds were very light, there were no waves, and lake currents in the study area were <0.1 kts flowing shore parallel to the NW.

3.1.2 Shipboard Tracking September 24, 1976

The cloud that resulted from the tracers release and subsequent mixing by the passing ore carrier was mapped four times in the next 10 hr and over 1300 15-mL water samples were collected. Figure 3.2 is a plot showing the

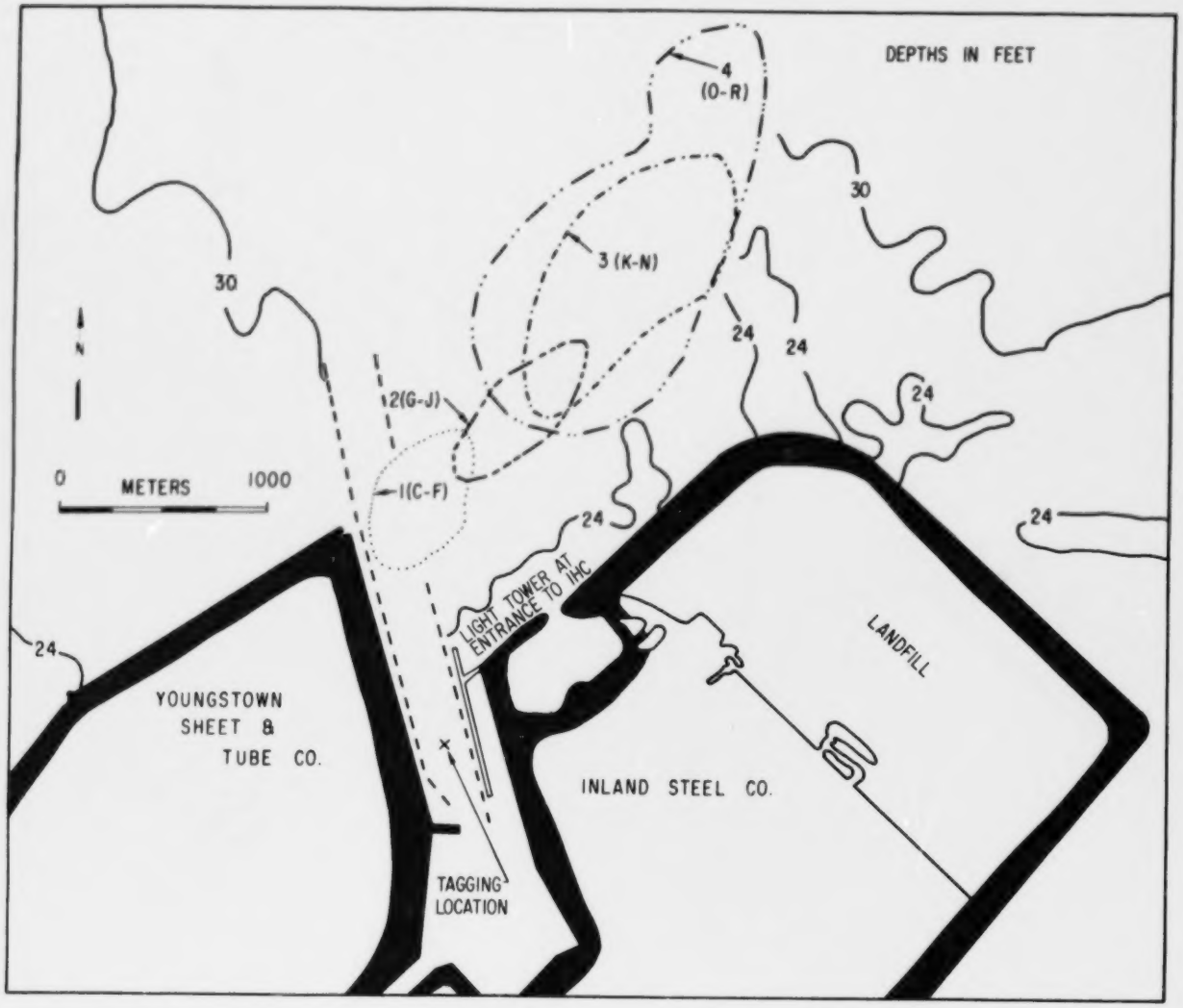

Fig. 3.1. REE Tagging Location and Contours of Lowest Detectable Amount of Dy that was Contoured for Plume Mappings 1-4, Floating-Plume

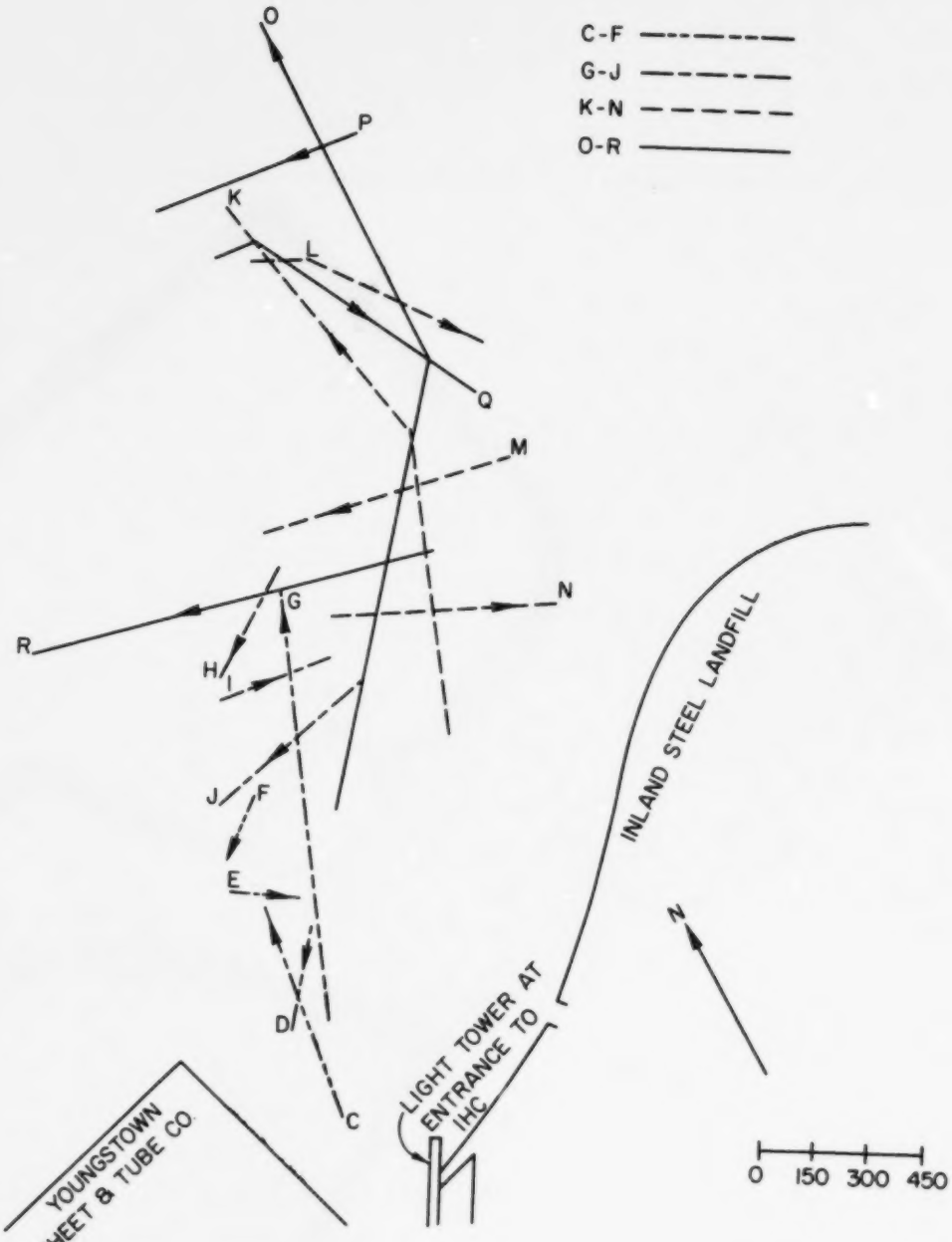

Fig. 3.2. Positions of Sampling Transects - Floating Plume (Direction of Boat Travel Indicated by Arrows)

sampling transects for the floating plume. The ends of each transect correspond to the first and last sampling locations in the transect. The arrow on each transect indicates direction of boat travel. Table 3.1 lists the sampling times, depths, and number of samples drawn for the transects shown on Fig. 3.2. Plan view contour plots of Dy and Sm concentrations at each sampling depth are shown in Appendix A. The fluorescent dye was used only as an indication of where to sample for the Dy and/or Sm, and thus no dye concentration records were recorded.

3.1.3 Data Analysis

About 800 of the collected water samples were analyzed by neutron activation. Generally, the sample that was collected at the surface in the middle of each transect was analyzed first. The order in which the remainder of the samples were analyzed was from the center of the transect outward until relatively little Dy or Sm was detected in the samples. The same process was followed at the other five depths. The only exception to the above selection process was Transect 0 (60 stations) where every fourth sample was analyzed.

The raw data, the net number of counts in the Dy or Sm peak, were extracted from the multi-channel analyzer by one of the two modes discussed in Sec. 2.1.4.1. Computer cards were punched from the raw data and computer graphics was used to post all the Dy or Sm counts from a given depth at correct relative locations for each of the four separate plume mappings (Table 3.1). This process was repeated for each depth. The resulting plan-views of tracer counts were contoured by hand in convenient intervals as dictated by the raw data.

A transparent, rectangular grid was then placed over the contoured raw data. The plan-view maps of the plumes thus were divided into about 40 rectangles of equal area. A visual estimate was made of the average number of net counts in a square and that estimate was punched onto computer cards. A short Fortran program was written and used to calculate:

1. Total amount of tracer in each plume (1-4) inferred from the analyzed samples,

Table 3.1. Log for Shipboard Activities, Summer Floating Plume, September 26, 1976

Activity	Time (hr CDST)	Transect	Sampling Depths (meters below surface)	# Stations in Transect
Tracer Dumped	0815-0835			
Plume 1 [C-F]	0933-0939	C[a]	0, 0.5, 1.0, 1.5, 2.5, 3.5	5
	0954-0958	D	" " "	5
	0959-1002	E	" " "	5
	1004-1006	F	" " "	5
Plume 2 [G-J]	1052-1106	G	" " "	9
	1112-1116	H	" " "	9
	1119-1124	I	" " "	8
	1130-1137	J	" " "	9
Plume 3 [K-N]	1320-1342	K	" " "	10
	1346-1353	L	" " "	12
	1359-1411	M	" " "	14
	1420-1427	N	" " "	12
Plume 4 [O-R]	1608-1646	O	" " "	59
	1700-1706	P	" " "	13
	1711-1721	Q	" " "	20
	1729-1740	R	" " "	18
			Total Stations =	213
			@ 6 samples/station	
			Total Samples =	1278

[a]See Fig. 3.1 for location of Transects.

2. The position of the center of mass of each layer,*
3. The variance about this center of mass in each layer, and
4. The amount of tracer in each layer.

3.1.4 Horizontal Migration of the Cloud

Figure 3.1 is a plot showing the contour of the lowest Dy concentration that was contoured for the four plume mappings. Note that clouds 1 and 2 are in a relatively protected zone behind the Inland Steel Company's landfill but clouds 3 and 4 are in the unprotected lake.

3.1.5 Diffusion Coefficients

Diffusion coefficients were calculated using elapsed time and observed variance for the last two cloud mappings [3(K-N) and 4(O-R)] at the 0.5 m level. These two mappings were in Lake Michigan proper and thus would be subject to lake-type diffusion. The calculated horizontal diffusion coefficients are shown in Table 3.2 with appropriate values reported by Murthy (1976) for Lake Ontario. With one exception (K_y-Sm), the values are very similar. The reason that the K_y for Sm is different by about an order of magnitude is probably because the Sm in cloud O-R is approaching minimum detectable amounts and the corresponding statistical error is high. The calculation of diffusion coefficients was done only to show that our data are reasonable when compared to data resulting from other tracing methods.

Table 3.2. Calculated Horizontal Diffusion Coefficients (m^2/s)

	Dy/Oil		Sm/Water		Murthy's Values[a]	
Time	K_y[b]	K_x[c]	K_y	K_x	K_y	K_x
2.5×10^4 sec	2.2	8.4	0.2	6.9	1.5	10.5

[a]Lake Ontario
[b]Longitudinal
[c]Lateral

*The layers were 0-0.75, 0.75-1.25, 1.25-2.0, 2.0-3.0, and 3.0-4.0 m (results from the surface sampler were not used due to sampler calibration problems discussed in Sec. 2.1.3.1).

3.1.6 Average Concentration

Figure 3.3 is a plot of the Dy/oil concentration (Kg/m^3) averaged over the horizontal extent of the measurable cloud for each depth sampled. Table 3.3 lists the elapsed time after tagging, the percent of original Dy that was accounted for in each plume, the average concentration integrated over the depth, and the dilution ratios as compared to Plume 1.

3.1.7 Percent of Dy and Sm above 1.25 m as a Function of Time

The percent of the total Dy/oil and Sm accounted for that is above 1.25 m plotted vs. time after tracer release is shown in Fig. 3.4. The separate cloud mappings are indicated by the times on the bottom horizontal axis and the transition from the area protected by the Inland Steel Landfill to the nearshore zone of Lake Michigan is indicated by the vertical dashed line.

3.2 FLOATING-PLUME DISCUSSION

3.2.1 Dy Tracer Loss from Oily Waste

The Dy loss factor (4×10^{-1}% Dy lost/mL oil/mL water) that was determined from the bench testing and discussed in Sec. 2.1.2.2 may be used to estimate if Dy losses were significant during the floating-plume study. The Dy is detected in plume 3 over a volume of 1.6×10^9 L (400m x 1000m x 4m). That volume would indicate only a 4% loss of Dy from the oily waste. Therefore, the loss of Dy from the oily waste into the water through cloud 3 is not thought to be significant.

In cloud 4, Dy can be detected over a volume of 6.2×10^9 L (600m x 2400m x 4m) for a maximum Dy loss of 15%. It is doubtful if even a 15% loss would significantly affect the trends exhibited by the results.

Note that the Dy tracer loss from the oily waste discussed above is not necessarily related to the percent Dy accounted for in Table 3.3. If some of the Dy were lost from the oily waste it could remain in nearby waters and thus be sampled and detected.

Table 3.3. Floating Plumes 1-4 Average Concentration Parameters

Plume	Elapsed Time After Tagging (Sec)	% Dy Accounted For	Average Concentration Over the Depth (Kg/m^3)	Dilution Compared to 1
1	4.8×10^3	131	4.8×10^{-7}	
2	1.1×10^4	83	4.6×10^{-7}*	≈ 1:1
3	2×10^4	77	2.2×10^{-7}	2:1
4	3×10^4	67	4.9×10^{-8}	10:1

*Plumes 1 and 2 were too close in time to significantly distinquish between them.

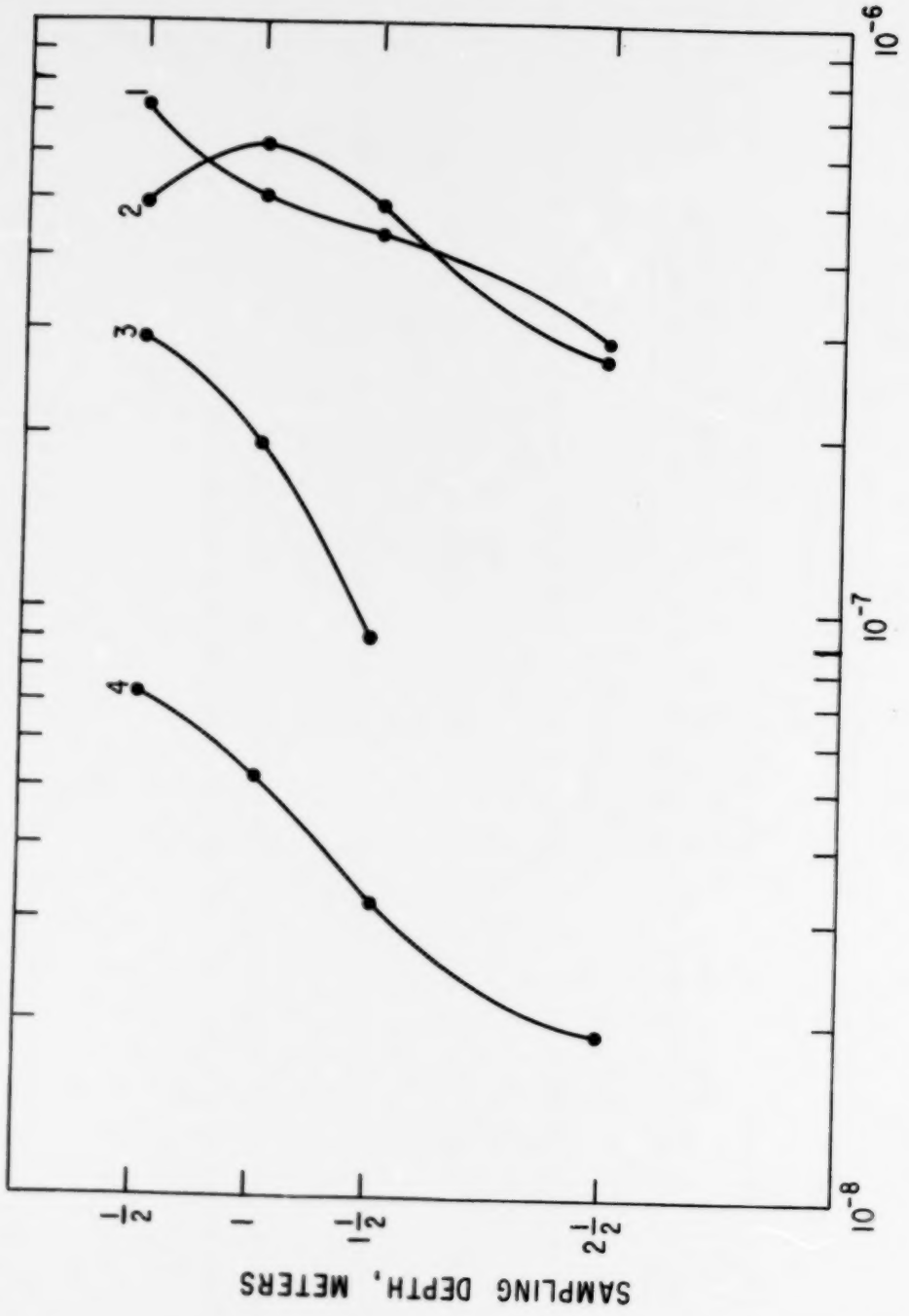

Fig. 3.3. Average Layer Concentration (Kg/m^3) of Dy/Oil Over the Measurable Cloud

The "percent Dy accounted for" was determined by integrating the concentrations at sampling points over the three-dimensional structure of the measurable plume and comparing that weight with the original amount of Dy in the oil spilled. Deviations from 100% are probably due to the sampling grid spacing and the diffusion of Dy to undetectable concentrations at the plume edges. Plume 1, which shows 131% of the original Dy accounted for appears strange but the seeming disparity is due to the non-synopticity of measurement of that plume. Plume 1 was sampled in a region where the flow of the canal was relatively fast and the direction of movement was changing from directly out the canal to a more lakeward heading. Consequently, plume 1 was the least synoptic of the four measured plumes.

3.2.2 Vertical Migration of the Cloud

Figure 3.4 shows that the amount of Dy and Sm above 1.25m changes with time and horizontal position. Both Sm and Dy migrate toward the surface until the cloud passes into the nearshore zone of Lake Michigan. After passing into the nearshore zone, the cloud tends to mix downward.

The warm canal water flows out and rises over the inflowing, colder Lake Michigan water. When the IHC plume enters Lake Michigan proper, it is then subjected to large-scale, lake-type diffusion and it is more dense due to cooling. These two factors, large-scale diffusion and the decrease of the density difference between the two layers due to cooling of the upper layer, cause some downward migration of the cloud when it enters the lake proper.

Initially, it was thought that the oily waste would resurface even after the extreme downward mixing that occurred due to the passing ore carrier; however, (in light of the data) it was hypothesized that the oily waste must have been reduced in size to oil droplets that were so small that positive buoyancy was less important than lake diffusion acting to mix the oil droplets. Recent literature was reviewed to see if others have found evidence of oils remaining suspended in the water column.

McAuliffe (1977) interpretated findings by others and reported that, "under agitation by wind and waves, many oils break up, and small droplets disperse into the underlying waters" and "as surface slicks break into oil droplets or particles and disperse in near-surface waters, most remain

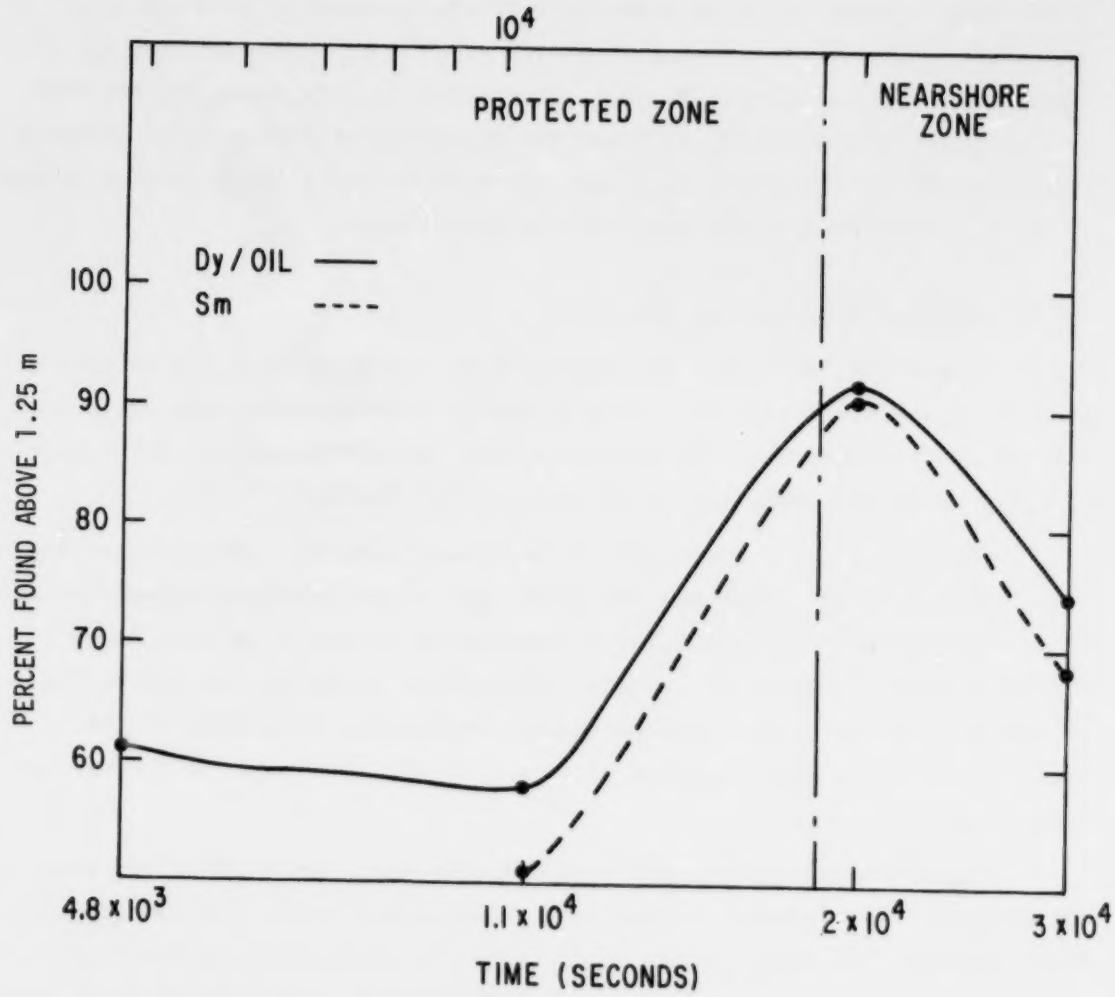

Fig. 3.4. Percent of the Total Dy/Oil and Sm Accounted for by Measurement, Found Above 1.25 m vs. Time After Tracer Release

suspended and move with the water." Certainly, the agitation caused by the passing ore carrier was equivalent to severe agitation by wind and waves and thus explains why the oil was found at depth and why the oil did not immediately resurface but moved with the water.

The explanation of why the oil did not resurface is related to the oil particle size after agitation. Shaw (1977), in a discussion on colloidal hydrocarbons says, "Larger oil particles rapidly float to the surface, as described by Stoke's law, when mixed into water. Colloids, however, remain in suspension for extended periods." Colloidal particles are roughly 10^{-9} to 10^{-6} m (1 nm to 1 μm) in size. Shaw goes on to say, "Evidence is indirect but substantial that colloidal size hydrocarbon particles are formed in seawater under conditions of turbulent mixing,...." The results of Peake and Hodgson (1966, 1967) and Gordon et al. (1973) were discussed by Shaw. Both groups mixed hydrocarbons with water and, "...found that the quantities of hydrocarbons less than 1 μm, as determined by filtration, were greatly in excess of the values for a saturated solution."

The final bit of evidence comes from McAuliffe (1977) who discussed the work of Brown et al. (1973), Brown and Huffman (1976), and Brown and Searl (1976). They measured non-volatile hydrocarbons along tanker routes in the Atlantic, Pacific, Indian, and Caribbean and determined that, "concentrations at 10 and 30 m were about 40% of those in surface samples. This indicates the hydrocarbons are particles (droplets?) and not in solution."

3.2.3 Relationship Between the Movement of the Oily Wastes and the Underlying Waters

After the oily wastes were mixed into the water column their movement did not differ significantly from the underlying Sm-tagged waters. As indicated in Sec. 3.1.5, mixing coefficients for the Dy/oil and Sm/water are similar. Moreover, Fig. 3.4 indicates no significant differences in the gross vertical movement of the Sm/water and Dy/oil. There is clearly a difference between the small, limited spill (57 L) artificially mixed into the water column discussed in this study and a major spill involving millions of liters. Extrapolations from the results above to the case of a major spill may not be valid. Therefore, different relative motions between the oil and underlying water might be expected for a major spill. This would be particularly true

during the initial phases of spreading of a major spill where gravity, viscosity, and surface tension are dominant. However, when such a slick becomes thin and oil mixes into the water column behavior similar to that reported in this study might be found.

4 RESULTS AND DISCUSSION--SINKING PLUME

4.1 WINTER SINKING-PLUME RESULTS, MARCH 2-4, 1977

4.1.1 Tagging Operation, March 2, 1977

IHC water was tagged *in situ* with 13.6 kg (30 lb) of samarium that had been complexed with DTPA, and with 7.5 kg of rhodamine WT dye. Volumes released were 114 L (30 gal) of samarium/DTPA solution and 38 L (10 gal) of rhodamine WT solution, respectively. The samarium/DTPA/Rh-WT tag was dispersed in IHC water by pumping the tag through a pipe with small holes drilled along one side. The pipe was lowered over the rail of the boat and the samarium solution was pumped into the pipe and dispersed at various depths between the surface and -1.0 m through the holes in the pipe. The dispersion process required 10 min and occurred at the "REE tagging location" (Fig. 3.5). On March 2, 1977, the tagging location was approximately 900 m upflow from the point where the canal water was sinking. The zone of convergence of canal and lake water was easily determined with a temperature probe and is indicated in Fig. 3.5 by "surface temperature convergence." As the survey vessel NEPTUNE proceeded lakeward in the canal, the surface water temperature dropped from 7.5 to 1.8°C within a few meters. Canalward of the sinking zone, the water temperature was vertically isothermal. Just lakeward of the sinking zone, however, the temperature profile showed warm (≈4.0°C) water near the bottom, overlain by colder (≈1.8°C) water.

The Dy-tagged, simulated oily waste was poured on the surface of the IHC effluent at the same time and in the same location that the *in situ* water tag (Sm) was injected. The oily waste and tracer consisted of 170 L of the waste mixed with 1.4 kg (3 lb) of Dy. The Dy had been dissolved in a 50% acetic acid solution.

4.1.2 Shipboard Tracking, March 2-4, 1977

About 1000 water samples were collected in Polyvials aboard the NEPTUNE while tracking the dye that was used to tag the IHC effluent. Pertinent water-sampling parameters such as time, date, and depth are shown in Table 4.1 and sampling transects are plotted on Fig. 4.1. Approximately 200 of the samples were collected in Transects A, B, and C (Fig. 4.1) in the

Table 4.1. Log for Shipboard Activities, Winter Sinking-Plume Study, 1977

Day	Date	Time (hr CST)	Activity	Sampling Depths (meters below surface)	No. Stations in Transect
Wed.	2 Mar.	1300-1310	Tracer dumped		
"	"	1806-1823	IHC Transect A[a]	0,1,4,7,B[b]	18
"	"	2015-2025	" " B	0,1,4,7,B	11
"	"	2226-2040	" " C	0,1,4,7,B	13
Thurs.	3 Mar.	0408-0424	Cal. Hbr. " D	0,0.5,3.5,6.5,B	7
"	"	0424-0426	" " " E	" " " " "	7
"	"	0430-0447	" " " F	" " " " "	17
"	"	0449-0455	" " " G	" " " " "	6
"	"	0505-0508	" " " H	" " " " "	3
"	"	0509-0528	" " " I	" " " " "	17
"	"	1246-1316	" " " J	" " " " "	15
"	"	1345-1401	" " " K	" " " " "	17
Fri.	4 Mar.	1057-1127	" " " L	0,1,4,7,B	28
"	"	1214-1228	" " " M	0,0.5,3.5,6.5,B	17
"	"	1504-1516	" " " N	0,1,4,7,B	6
"	"	1516-1556	" " " O	0,1,4,7,B	17
"	"	1652-1706	" " " P	0,1,4,7,B	7

[a]See Fig. 4.1 for location of transects

[b]B-Bottom

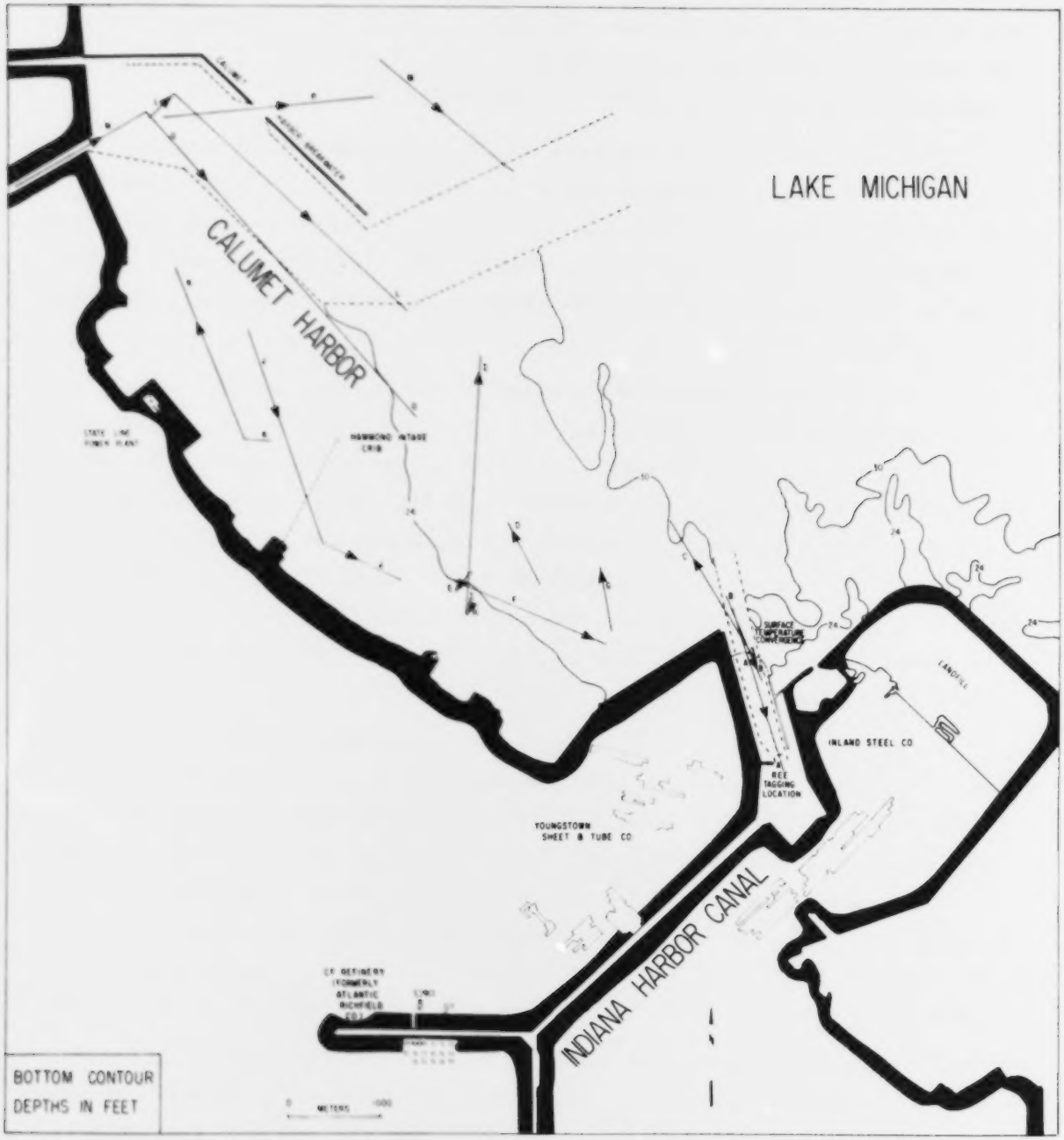

Fig. 4.1. REE Tagging Location, Temperature-Convergence Zone, and Positions of Sampling Transects, Sinking-Plume

canal-entrance and near-entrance areas. All 200 were analyzed by NAA for their Dy and Sm concentrations. Of the remaining 800 samples collected in the Calumet Harbor area, 350 were analyzed* and only ten of those indicated the presence of Sm (canal water); however, many of the samples from Calumet Harbor indicated the presence of Dy (simulated oily waste).

In Figs. 4.2-4.7, the sampling stations are numbered in ascending order corresponding to the direction of boat travel. The transect locations are plotted on Fig. 4.1. Each transect (on Fig. 4.1) has an arrow indicating the direction of boat travel and the ends of each transect correspond to the first or last sampling station. The distance between sampling stations varies slightly but is ≈100 m.

Contours of constant concentration values in Figs. 4.2-4.7 are in nanograms per liter (ng/L); that is 10^{-9} g/L. The Dy-concentration contour interval is based upon a two-standard-deviation spread (statistically, the 96% confidence level) in the net number of counts in the peak. This spread is close to 100 counts. Thus, each ng/L contour interval on Figs. 4.2-4.7 reflects a 100-count interval in the raw data. Owing to rounding, and significant-digit considerations, the conversions from counts to ng/L may give nonuniform differences in contour values. Note that 100 counts corresponds to the minimum detectable amount of Dy or Sm.

Figures 4.3-4.7 show, in addition to the Dy concentration, the near-bottom dye concentration. The dye was used merely to indicate the presence of IHC effluent and exact correspondence between the concentrations of the Dy and dye should not be expected. The Dy values on Figs. 4.3-4.7 represent "instantaneous" values, inasmuch as they were determined from 15-mL grab samples. The dye values represent integrated averages over a much larger flow of water (≈125 mL/s) and a much longer time period. The purpose of monitoring the dye was to indicate water masses to be sampled for Dy and Sm.

Figure 4.2 is a plot of the Dy concentrations (oily-waste tag) with depth in Transect A (Fig. 4.1). Transect A passed directly through the strong surface-temperature gradient at the mouth of the IHC, and Fig. 4.2 clearly shows a zone of sinking Dy (between Stations 1 and 6) and a region of high

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*That is, every other or every third sample along a transect was analyzed (unless a high value was observed, in which case samples on either side were analyzed).

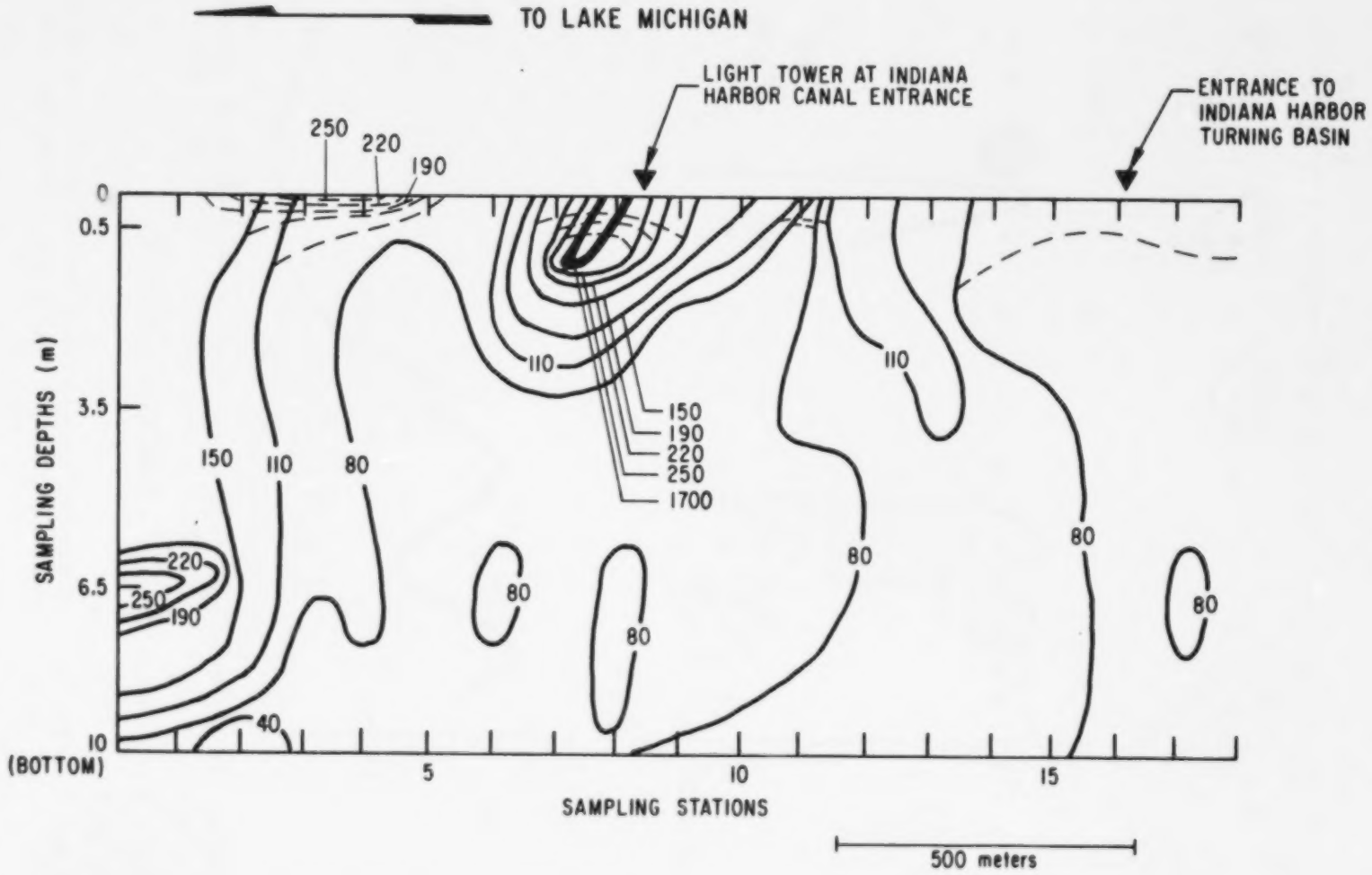

Fig. 4.2. Transect A: Dy Concentrations. (Concentrations in ng/L All 90 samples collected were analyzed. The dashed contours indicate how the figure would look if concentration values for the surface samples could have been considered.)

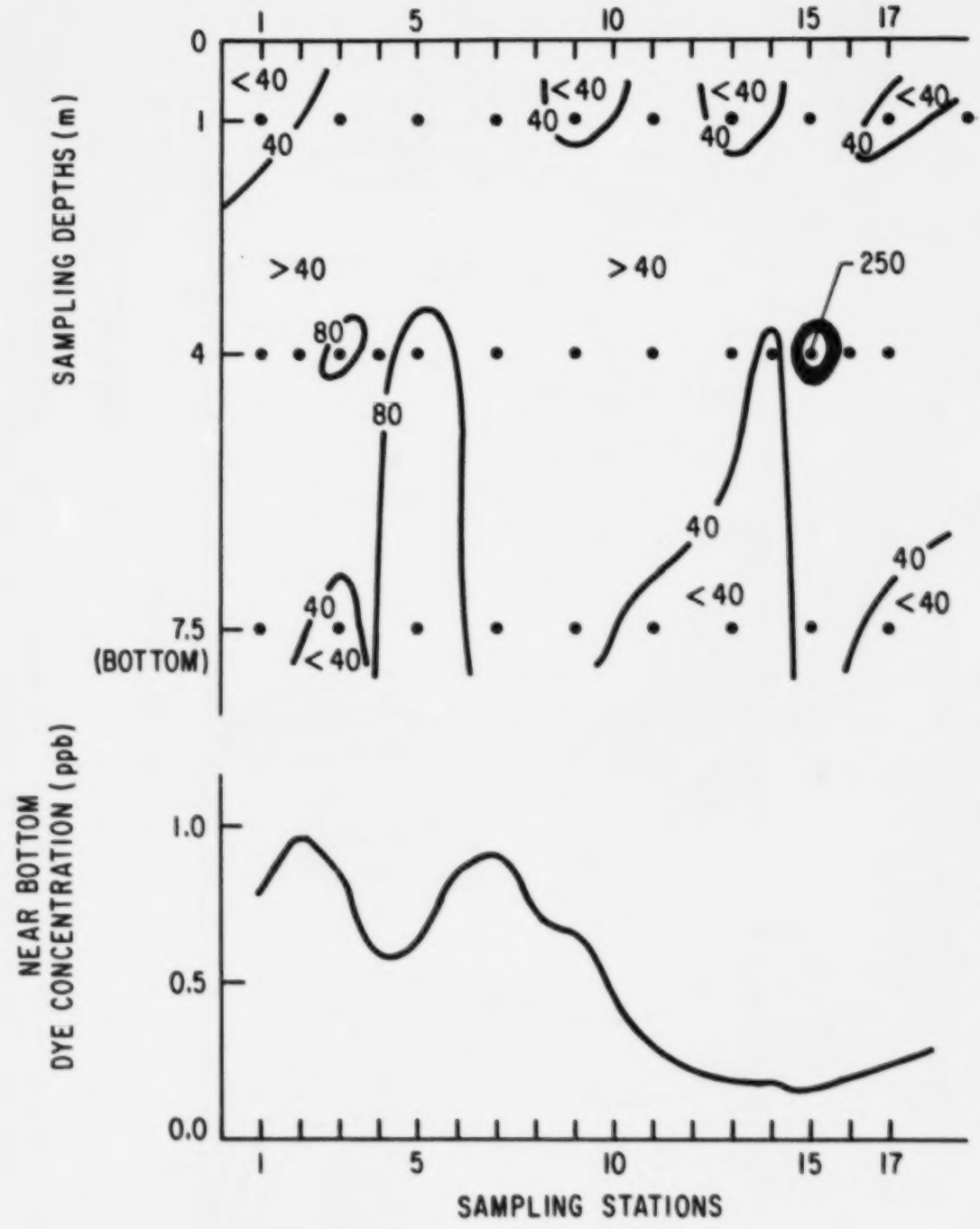

Fig. 4.3. Transect F: Dy Concentrations and Near-Bottom Dye Concentrations (dot indicates sample analyzed at that point, Dy concentrations in ng/L)

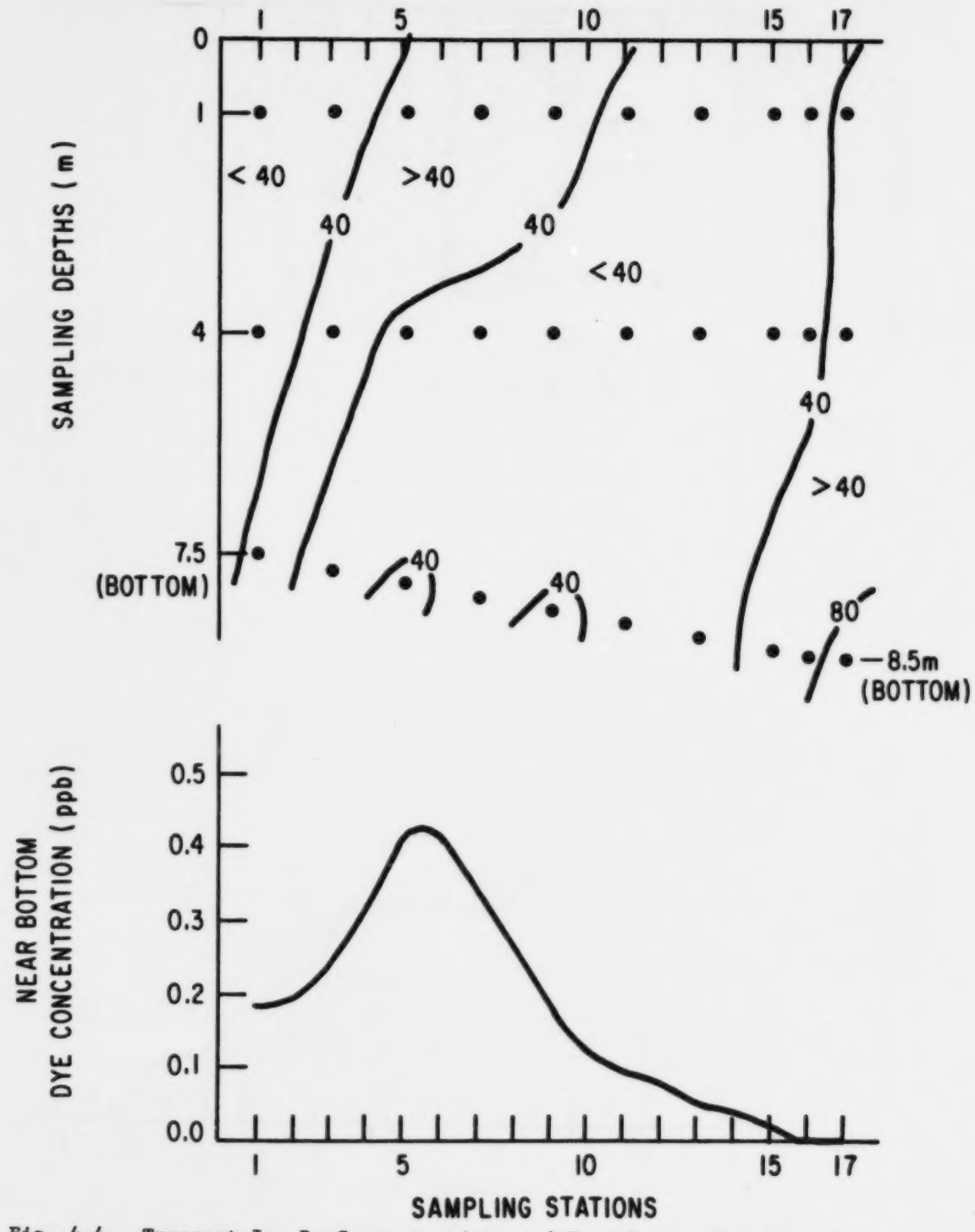

Fig. 4.4. Transect I: Dy Concentrations and Near-Bottom Dye Concentrations (dot indicates sample analyzed at that point, Dy concentrations in ng/L)

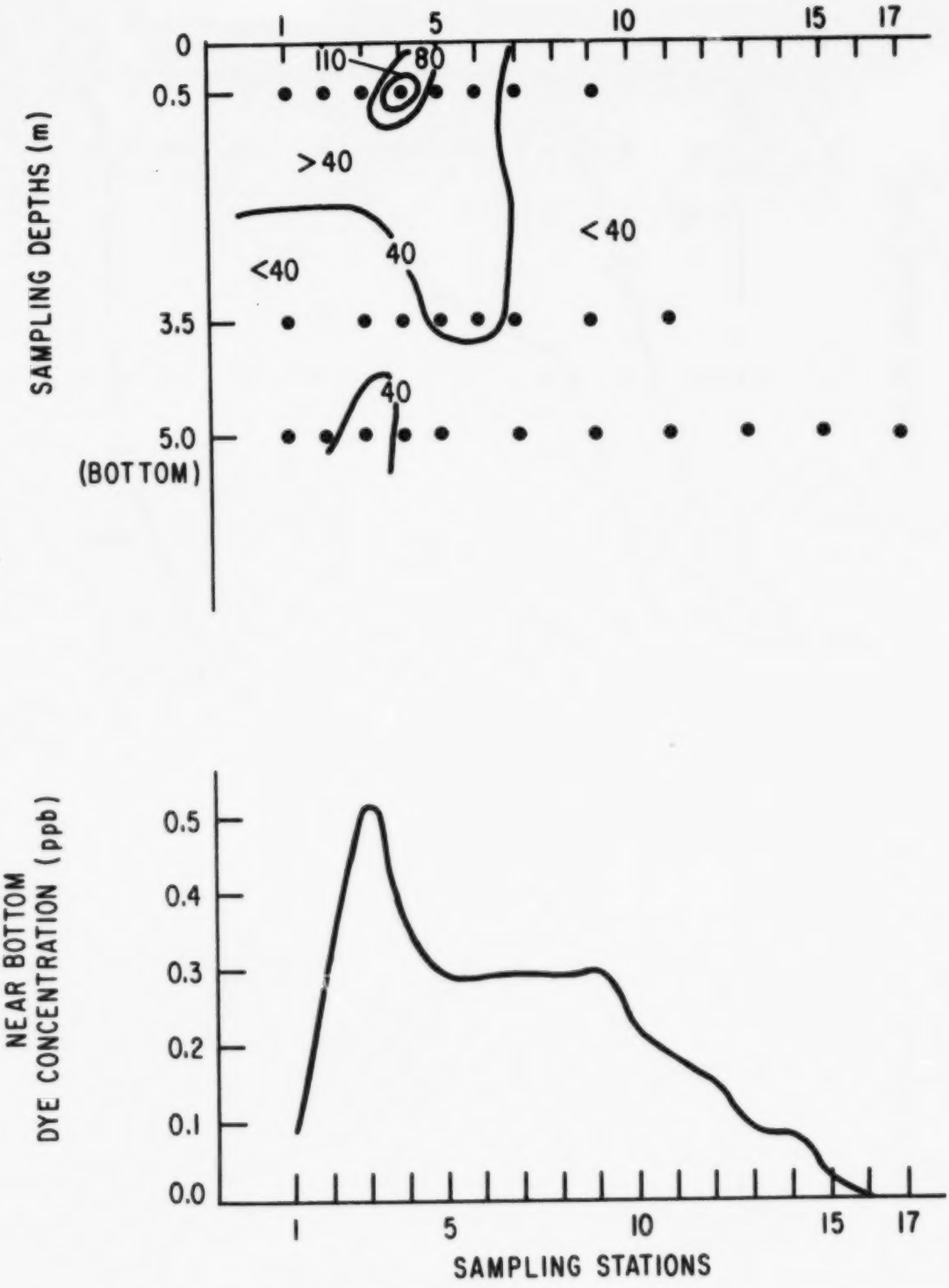

Fig. 4.5. Transect K: Dy Concentrations and Near-Bottom Dye Concentrations (dot indicates sample analyzed at that point, Dy concentrations in ng/L)

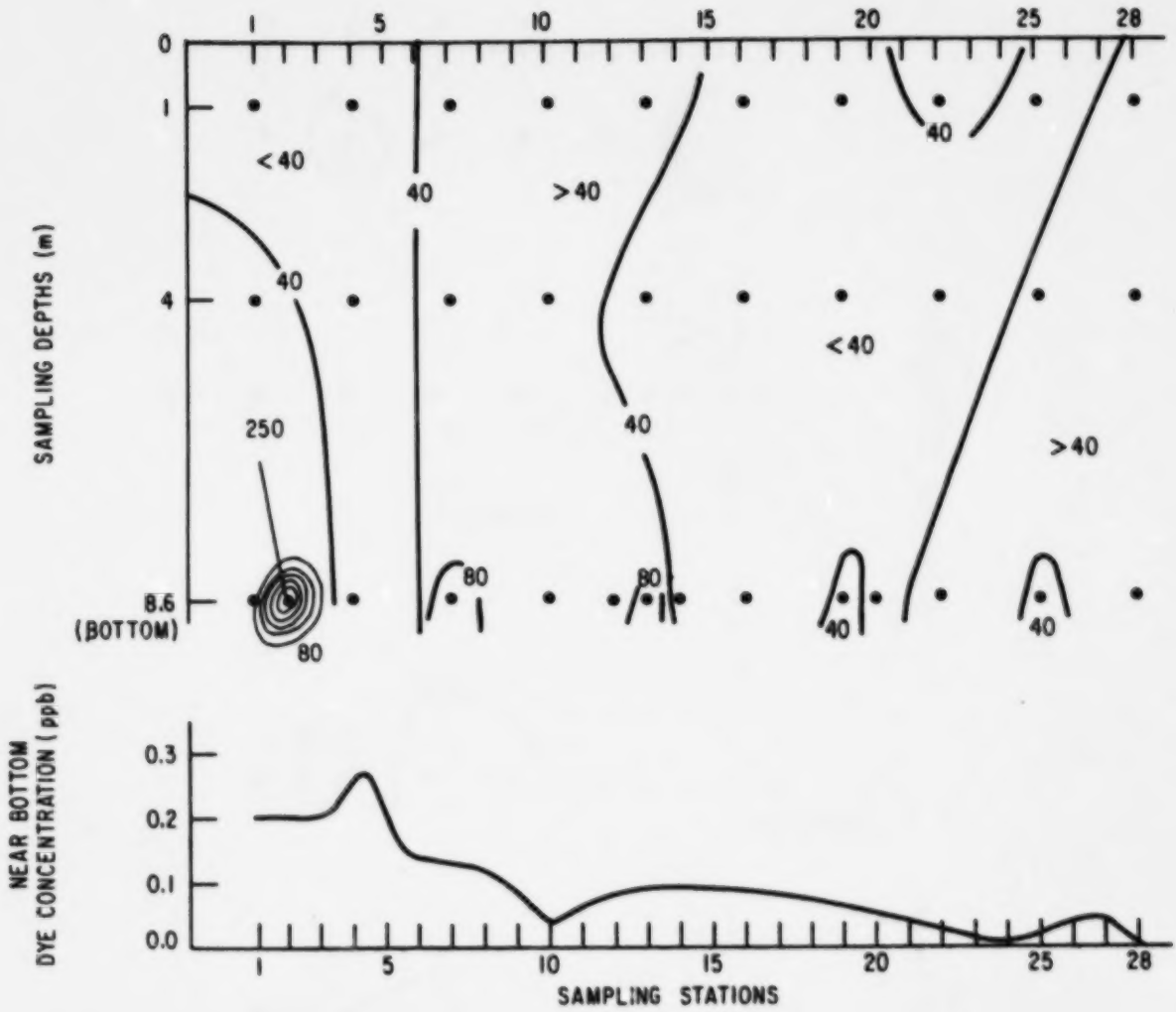

Fig. 4.6. Transect L: Dy Concentrations and Near-Bottom Dye Concentrations (dot indicates sample analyzed at that point, Dy concentrations in ng/L)

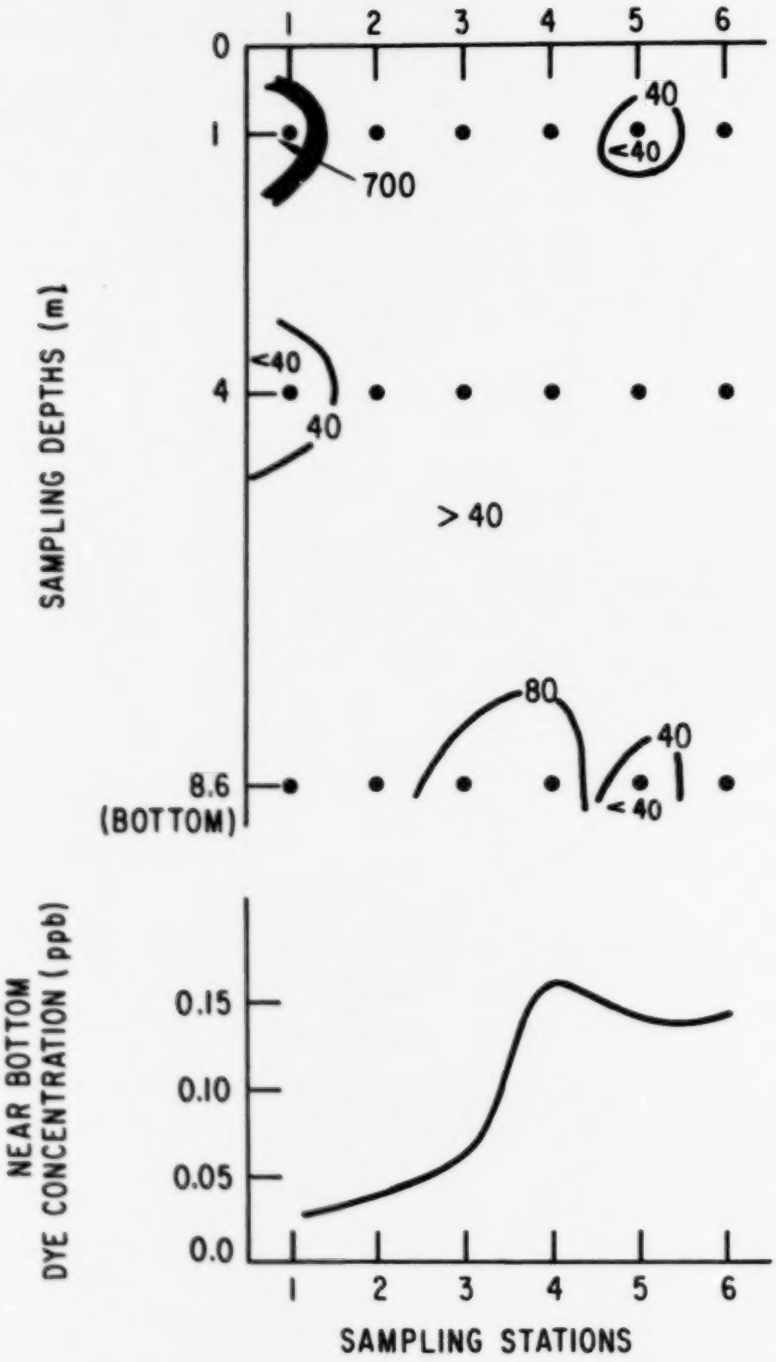

Fig. 4.7. Transect N: Dy Concentrations and Near-Bottom Dye Concentrations (dot indicates sample analyzed at that point, Dy concentrations in ng/L)

Dy concentration near the bottom. Thus, Fig. 4.2 shows the sinking of the simulated oily waste; however, the dashed contours, which indicate how the raw data would have been contoured if the results of the uncalibrated surface sampler (Sec. 2.1.3.1) were considered, suggest that some of the oily waste does cross the subduction zone and does not sink.

Dy transects B and C and Sm transect A, B, and C are shown in Appendix B. The Sm transects show little similarity to Dy transect A. Diffusion calculations for the Sm tracer in the canal (Sec. 4.2.3.2) indicate that the Sm plume had diffused considerable less than expected from its initial size at tagging (24m x 2m x 1m) while traveling to the subduction zone. Consequently, the main body of Sm was missed during the sampling of transect A but the main body of the Dy-tagged oil which had spread over the canal surface to a much greater extent, was sampled. Transects B and C occurred after most of the tracer had left the canal. In fact, the plume, as indicated by the dye, was lost for about 8 hrs and transects B and C were made during this period in the hope of relocating the main body of the plume. A portion of the plume was relocated in the region of transects D-I (Fig. 4.1); however, a partitioning of the Dy/oily-waste and Sm/water had occurred prior to relocation. This partitioning is discussed in detail in Sec. 4.2.3.1.

Figure 4.3, for Transect F (Fig. 4.1), shows both the Dy concentrations through the water column and the dye concentration near the bottom. Along this transect, the simulated oily waste and its Dy tag seem to be relatively well mixed with depth. There is one sample point with a very high Dy concentration; the high value may be due to an unusually large drop of oil drawn through the sampling tubes. These singular spots of high concentration occur in many transects.

Figure 4.4 for Transect I, shows a relatively high concentration of Dy at the lakeward end of the transect. Again, the Dy/oily-waste appears to be relatively well-mixed, as in Transect F. A peculiar occurrence in Transect I is that the dye does not reflect the increasing Dy/oily-waste concentration at the lakeward end of the transect.

Transect K data (Fig. 4.5) reveal the close proximity of the oily waste to the shore. Figure 4.1 shows that the NEPTUNE steamed obliquely into and then away from shore. The region of highest concentration was only about 500 m from shore. Concentrations may have been higher further inshore, but, because of the shallow depth, the NEPTUNE could not sample there.

Transect L (Fig. 4.1) was made by steaming southeastward along the centerline of the dredged ship channel, which runs parallel with the Calumet Park Breakwater. Concentrations (Fig. 4.6) along this transect show that the Dy/oily waste, and the dye, made a clockwise circuit of the Calumet Harbor, because no dye had been detected in the channel on the previous day.

Transect N (Fig. 4.1) was made by steaming out of the Calumet River, starting about 900 m upstream of the river entrance. The Dy data (Fig. 4.7) indicate that some of the oily waste from the IHC entered the Calumet River. Stations 1-4 (Station 4 is at the river entrance) were in the river, and there were detectable amounts of Dy at those stations.

Plots of the remaining transects D, E, G, H, J, M, O, and P are shown in Appendix B because they provide little additional information.

4.1.3 Tracer Concentrations at the SWFP

Some 240 Polyvial water samples were drawn at the SWFP from the raw water streams of the shore and crib intakes. All 240 samples were analyzed by NAA, and concentration data for the samples that contained Sm and/or Dy are shown in Tables 4.2 and 4.3. For all the samples that contained detectable Sm and/or Dy, Fig. 4.8 gives relative amounts as a function of time for each raw-water intake. Relative amount is computed as the amount of a given REE found in a Polyvial sample divided by the quantity of that REE was released in the IHC effluent times 100.

4.1.4 Lake Currents and Meteorological Conditions

4.1.4.1 Results of Lake Current Measurements

The current meters were deployed for this study for the period January 4 to March 26, 1977. All meters returned useful data, except the meter at Station II which had sporadic malfunctions. Data from that meter, when operating properly, were consistent with those at Station I but were not used in time-series analyses. The major features of the observed currents during the study period were:

1) the mean flow was toward the southeast, though there were four major direction reversals of the generally southeastward flow during the recording period;

Table 4.2. Sm Concentrations of Samples Collected at the SWFP

Date	Time, CST	Concentration,[a] µg/L	% error
		Crib Samples	
3 Mar.	2220	61.0[b]	2.0
"	2310	7.7[b]	8.3
4 Mar.	0030	2.8[b]	23
"	0300	6.7[b]	9.6
"	0430	102.1[b]	1.4
"	0450	6.1[b]	10
"	0720	2.4[b]	24
"	1040	5.0[b]	13
"	1200	2.1[b]	27
"	1220	5.1[b]	12
"	1520	1.6	34
		Shore Samples	
3 Mar.	2200	2.9[b]	22
"	2250	1.6	42
"	2340	4.0[b]	18
4 Mar.	0300	1.6	46
"	0450	1.6	41
"	0710	2.7[b]	25
"	1100	1.8	34
"	1200	1.9	32

[a]Minimum detectable amount, Sm - 100 counts = 1.4 µg/L

[b]Indicates average of two irradiations.

Table 4.3. Dy Concentration of Samples Collected at the SWFP

Date	Time, CST	Concentration,[a] ng/L	% error
		Crib Samples	
3 Mar.	2210	54	29
"	2230	82	20
"	2310	54[b]	29
"	2320	61[b]	27
"	2340	55[b]	30
"	2350	70[b]	24
"	2400	47	33
4 Mar.	0020	57	26
"	0030	60[b]	26
"	0050	43	36
"	0100	43	39
"	0110	43	37
"	0140	48	34
"	0400	51[b]	32
"	0710	45	33
		Shore Samples	
3 Mar.	2200	74[b]	21
"	2230	158[b]	14
"	2250	45	44
"	2300	48	39
"	2350	62	31
4 Mar.	0020	45	43
"	0050	74[b]	29
"	0100	46[b]	45
"	0120	64	32
"	0130	58	31
"	0220	48	40
"	0230	71	26
"	0250	67	29
"	0300	74	28

Table 4.3. (Contd.)

Date	Time, CST	Concentration,[a] ng/L	% error
		Shore Samples	
4 Mar.	0330	43	45
"	0410	52	36
"	0420	47	40
"	0430	69	27
"	0550	55	32
"	0630	49	36
"	0720	68	26
"	0730	55	31
"	0840	45	40
"	1010	64	28
"	1050	50	35
"	1100	62	28
"	1110	56	35
"	1240	49	36
"	1320	47[b]	35
"	1500	45	37
"	1520	62	27

[a]Minimum detectable amount, Dy - 100 counts = 43 ng/L

[b]Indicates average of two irradiations.

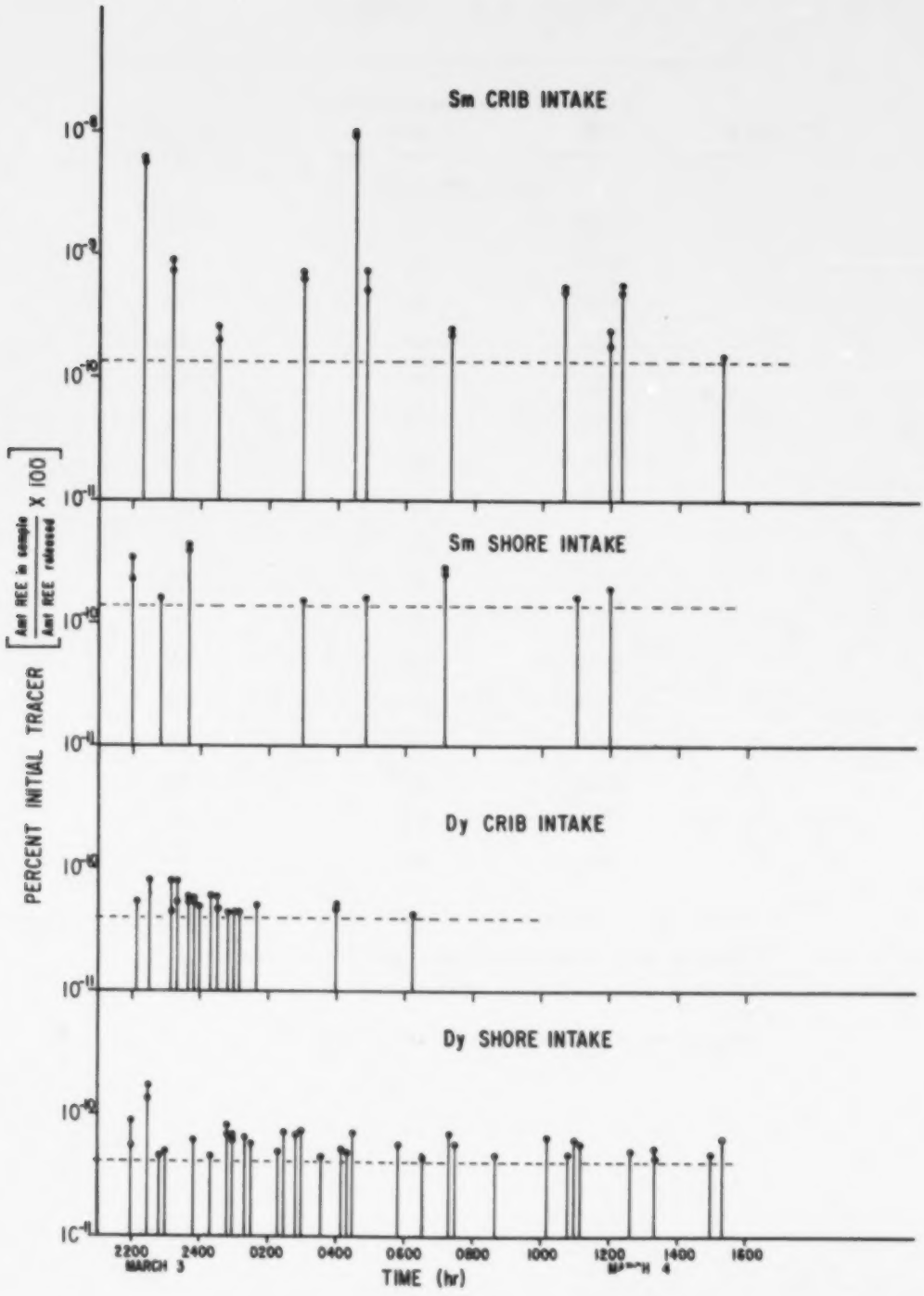

Fig. 4.8. Relative Amount of Sm or Dy in the Samples Collected at the SWFP as a Function of Time. (Dashed line indicates the minimum detectable amount; two dots at a sample indicate the sample was irradiated twice and shows the value of each irradition.)

2) the average speed was about 0.015 m/s and the rms speed was about 0.074 m/s;

3) most of the energy of the currents was in the low frequency region of the spectrum, between 1.0×10^{-6} Hz and 1.4×10^{-5} Hz;

4) the vertial variation of the current was small at Station I with a cross-correlation coefficient between the major velocity components at the two meters of 0.80; and

5) the currents at Stations I, III, and IV, when parallel to the depth contours, were relatively uniform with high coherence between currents at the different stations at frequencies below 1.4×10^{-5} Hz. Low coherence existed above that frequency, except at the frequency bands near 3.3×10^{-5} Hz and 1.3×10^{-4} Hz.

Although sampled only sparsely, the flow field seems to have been rather uniform over the region between the IHC and SWFP intakes. Near-bottom currents at Stations I, III, and IV were resolved into components parallel and perpendicular to the major axis of current fluctuations (the major axis was defined as that on which the cross-correlation coefficient of the two components at the single station was zero). Cross correlations were then calculated between the major velocity components of the three stations for about 22 days of the record. Similar calculations were made for the minor velocity components. The results of these calculations are shown in Fig. 4.9 where cross-correlation coefficients for the major and minor near-bottom velocity components between stations are given as a function of the spatial separation between the meters correlated. The circled points represent values from this study. The triangles represent values from data from another Argonne study in which current meters deployed at mid-depth were located along a northeasterly line (perpendicular to shore) between Stations I and III. These data, while not synoptic with those of the present study, indicate similar relationships but for separation distances along a line in the offshore direction. Major velocity components are well-correlated within the study area for the period of measurement and suggest the existence of a rather uniform flow field.

4.1.4.2 Meteorological Conditions

Figure 4.10 is a progressive-vector diagram of Midway Airport Winds during the sinking-plume study. The figure shows that the wind was from the SE from about 0800 hr on March 2 until about 0800 hr on March 4. Total wind

movement during the period of SE winds was about 10^3 km and maximum speed averaged over an 8-hr period (length of longest vector/8 hr) was about 6.5 m/s.

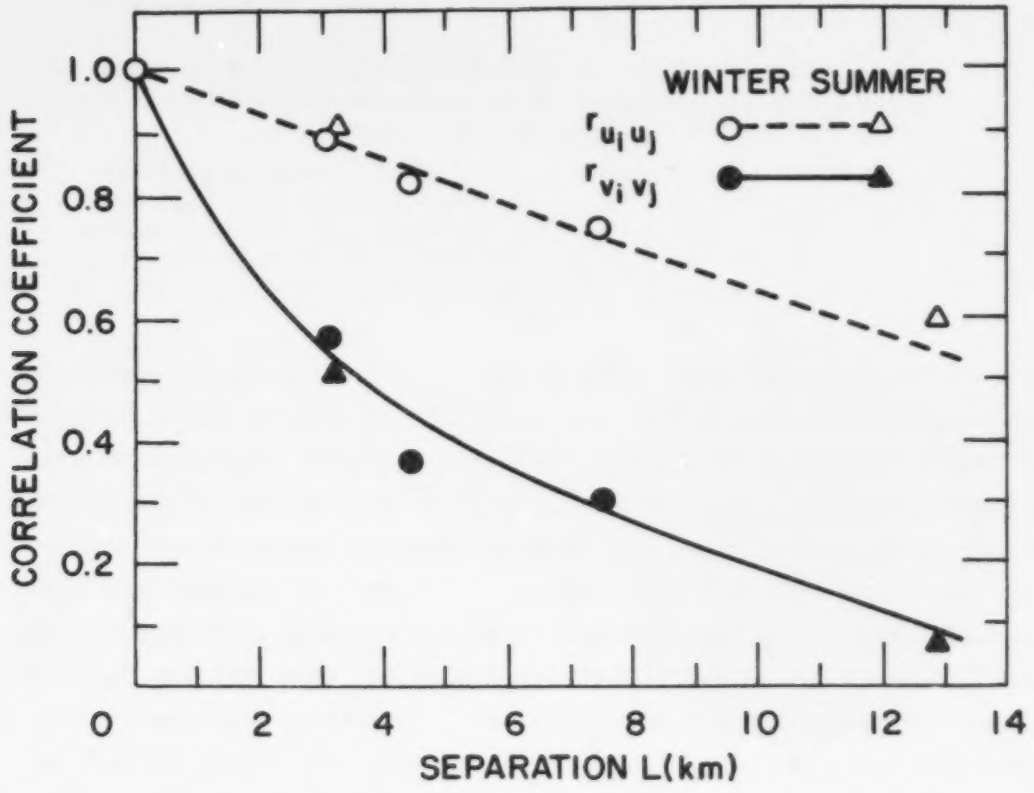

Fig. 4.9. Correlation Coefficients for the Principal and Transverse Components of the Current as a Function of the Distance Between Stations

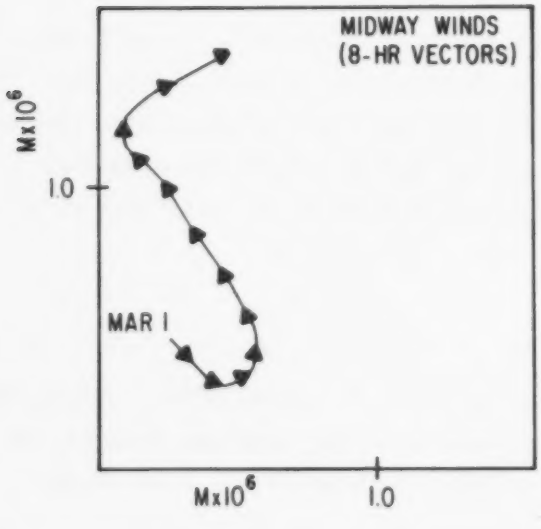

Fig. 4.10. Progressive-Vector Diagrams for March 1-4, 1977, Midway Airport Winds

4.2 SINKING-PLUME DISCUSSION

4.2.1 General Considerations

In this part of the report we examine and extend certain aspects of the above work involving the sinking plume. The results of the field experiment are summarized and employed to provide descriptions of the sinking plume behavior of the IHC effluent. Results of the tracer experiment, in which a portion of the IHC effluent was tagged, are compared with estimates of dilution using a similar turbulent-diffusion model to gain some understanding of the applicability of such models in the study region. Then, based on the characteristics of lake currents during the study period, a simple model is proposed to estimate the mixing by turbulent diffusion of the entire IHC effluent as it moves northwestward.

4.2.2 Characteristics of IHC Effluent Plume for January 4 - March 26, 1977

The South Water Filtration Plant's intakes are located at the shore near the plant, and at the Dunne Crib (Fig. 1.1). These intakes lie on a northwesterly bearing from the IHC. In order that the effluent from the IHC reach the SWFP's intakes, it must be advected by the nearshore currents in the lake. This section discusses the advection of the effluent and the dilution of the effluent as based on the random motions of the observed currents. This discussion is limited to the period January 4 - March 26, 1977. It should be remembered that the ice-cover observed during this period may not apply to other years, as this winter was the severest on record. The advection and dispersion physics, on the other hand, are generally applicable and may be used to deduce the expected transport and mixing of IHC effluent under similar wind and ice-cover conditions.

If the IHC effluent is to reach the intakes, a northward current along the shore is a necessary but not completely sufficient condition. The current must be of sufficient magnitude and persistence for the water to move the distance between the IHC and one or the other of the intakes. During the winter of 1977 such events were not common -- only four occurred. Each of these was marked by elevated levels of hydrocarbon odors in the raw water drawn in from the SWFP's intakes.

There were also several northward current episodes of lesser magnitude. Weak hydrocarbon odors were detected during these periods, but they were not significant. (The maximum level observed during one of these episodes was 4 Ch.*)

During March 8-10 an episode of generally westward flow occurred. The hydrocarbon-odor levels, generally low during the preceding days, were most likely the remnants of the March 2-4 episode. On March 9, a maximum hydrocarbon odor level of 7 Ch was reached at the shore intakes and on March 10 an odor level of 10 Ch was reached at the Dunne Crib.

Generally, hydrocarbon odors are not observed at the SWFP until northward-flowing currents have continued for about a day. Hydrocarbon odors then persist even after the current has reversed direction. The structure of the currents both before and after the northward-current episodes indicates that any tracer in the IHC effluent will tend to be confined to the shore region by the current field. Also, mixing will likely occur only slowly and will be due to advection of the surface waters offshore by wind along with the slow replacement by deeper water from the lake.

4.2.3 Transport and Dilution of Tagged IHC Effluent

4.2.3.1 Interpretation of Experimental Observations

Results of the plume-tracking field study (Sec. 4.1) show that the effluent from the IHC enters the City of Chicago's water-purification system at the SWFP's Dunne Crib and shore intakes. Unfortunately, a detailed picture of the effluent's path to the crib or shore intake cannot be established from the tracer data. However, two paths may exist for transport of IHC effluent to the SWFP's water intakes. Each path is governed by the nature of entry of IHC effluent into the lake, incompletely mixed near-surface water taking one path and well-mixed, 4°C bottom water taking the other.

During the development of a sinking plume, when the IHC waters mix with Lake Michigan waters at the subduction zone, not all the IHC water sinks to the bottom. If all the IHC water sank to the bottom, then the near-surface

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*Ch = "hydrocarbon" odor (Standard Methods for the Examination of Water and Wastewater, 1965, Table 18).

temperatures immediately lakeward of the convergence zone would be the same as ambient Lake Michigan water. But temperature profiles immediately lakeward of the convergence zone show the near-surface water to be 1-1.5°C, not near 0°C as is typical for ambient Lake Michigan water. Also, the data from the surface sampler in Fig. 3.6 indicates that some portion of the oily wastes do not sink but remain on the surface. Therefore, some portion of IHC water stays near the surface and moves toward the shore due to the action of winds blowing from the southerly quadrants. This is the portion of the IHC effluent that was tracked by the NEPTUNE, and it typically follows a path along the shoreline.

The other path, followed by the portion of IHC water that sinks to the bottom, roughly parallels the 9.1-m (30-ft) depth contour (Fig. 4.1). This isobath coincides with the lakeward end of the IHC entrance channel. Such bottom water from the IHC would move directly into the lake and then northeastward along the coast, missing the area enclosed behind the Calumet Harbor Breakwater. This sinking-plume portion of the IHC effluent would follow the second path to travel directly to the SWFP. Topographically, the depths of the crib intake and of the IHC entrance channel are about the same, 9.1 m (30 ft). Effluent flowing out of the IHC along the bottom would tend to remain near the 9.1-m (30-ft) contour as it moved northwestward parallel to shore, and this path would carry it directly to the crib intake. Further evidence of the existence of a direct lakeward path is found in the high concentrations of Sm detected in the crib samples and the fact that these samples were drawn at the time that the NEPTUNE was drawing water samples in Calumet Harbor, water samples that contained Dy (oily waste) but virtually no Sm (canal water).

The results from Transect I (Figs. 4.1 and 4.4), which ends near the 9.1-m (30-ft) isobath, indicate an increasing concentration of Dy in a lakeward direction, but no corresponding increase in dye. In approaching the 9.1-m (30-ft) isobath, the NEPTUNE may have entered a segment of the plume moving northwestward along the bottom. However, the fact that the dye concentrations do not reflect the increasing Dy concentrations is puzzling. Because the Dy-tagged oil spread over the surface of the canal much faster than the Sm- and dye-tagged water spread beneath the surface, the Dy-tagged oily waste reached the subduction zone first. Transect I may have reached

the leading edge of the tagged oily waste that had been mixed into the sinking plume before the Sm and dye became mixed.

Table 4.2 shows the Sm concentrations in the raw-water samples collected at the SWFP. Seven of the eleven crib samples contained higher concentrations of Sm than any of the eight shore samples. Two of the crib samples (March 3 at 2220 hr and March 4 at 0430 hr) contained very high concentrations of Sm. In contrast, fourteen of the crib samples contained Dy and all but two of these were in a three-hour-and-ten-minute span (2210-0120). Thirty-one of the shore samples contained Dy, however, and these were fairly equally spaced throughout the entire 17-hour sampling interval at the SWFP.

These results indicate that significantly more Sm (the water tracer) went to the crib intake than to the shore intake. Also, significantly more Dy (the oil tracer) went to the shore intake than to the crib intake. This appears reasonable, because a large portion of the oily waste (Dy) would tend to remain on the surface and thus would be blown toward the shore by the SE winds that occurred during the experiment. Therefore, the oily waste would have had a higher probability of being drawn into the shore intake. The water (Sm tracer), however, would be more likely to sink at the subduction zone and be carried along the 9.1-m (30-ft) isobath with the prevailing northwesterly directed current to pass over the crib's bottom water intake. As mentioned above, further evidence of this partitioning of the oily waste and IHC water is found in the fact that so little Sm (the water tag) was seen in the Calumet Harbor area.

A representation of the average current field for the near-bottom waters in the vicinity of the IHC and SWFP has been constructed from the current-meter records for March 3, 1977, as an aid in determining the path of the IHC and tagged effluents. This day was chosen because it coincides with the period of maximum current during the tracer experiment. The flow field is shown in Fig. 4.11. Streamline directions were drawn at the locations of the current meters and aligned with the average direction of current during the period. The spacing between streamlines was made inversely proportional to the observed average speeds. The current field was modified in the vicinity of the mouth of the IHC to reflect the outflow from the canal. This representation is clearly limited by the small number of data points; however, it does not appear to be inconsistent with other observations of the tracer transport.

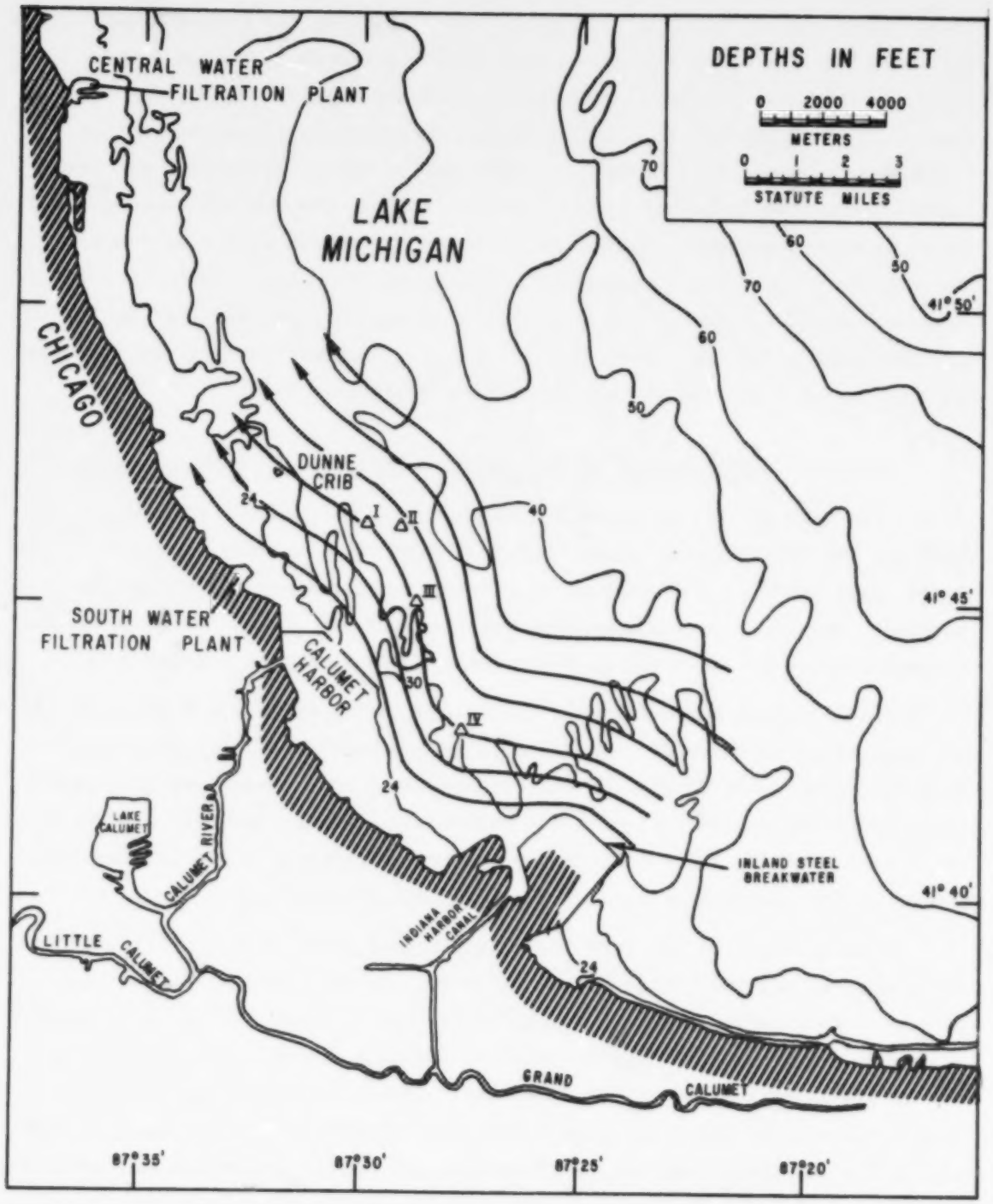

Fig. 4.11. Schematic Reconstruction of the Velocity Field of the Near-Bottom Water on March 3, 1977

Several features of the velocity field are shown in this representation. First, the turning of the current after passing the Inland Steel Breakwater will advect the IHC effluent into the nearshore region between the IHC and Calumet Harbor. This is a relatively shallow region that can experience considerable wave action under southeasterly or easterly winds. Strong mixing under such conditions would act to weaken or destroy the vertical stratification of the sinking plume. Second, the IHC effluent advected into the region between Calumet and Indiana Harbors must return to the lake. The only return paths are through the opening in the Calumet Harbor Breakwater or around the end of the breakwater. Third, the IHC effluent would, if there were no mixing across the streamlines, be confined to a narrow region near the shore as it passed the South Water Filtration Plant.

4.2.3.2 Comparison of Simple Dilution Estimates with Measurements

The lack of detailed sampling of the plume between the IHC and the SWFP and the partitioning of the tagged portion of the plume, described above, make definitive statements concerning the transport and mixing impossible. However, a simple estimate of the dilution of the tracer along an assumed pathway can be compared with tracer measurements at the SWFP.

Table 4.4 presents dilution ratios for the Sm samples collected during the experiment at the SWFP's crib and shore intakes. The dilution ratio is defined as the ratio of the initial concentration in the water at the tagging location to the concentration in the collected samples. Initially, 13.62 kg of Sm were mixed in the IHC waters over a region about 24 x 2 m in area and 1 m in depth, yielding an initial concentration of 0.284 g/L.

The estimate of the dilution of the tagged portion of IHC effluent between tagging and the intakes neglects several of the complexities of the process. Horizontal spreading of the tagged patch in the IHC is computed for the transport between the initial tagging location and the lake. Partitioning at the sinking location and additional mixing there are neglected. After sinking, the patch is assumed to be advected at an average speed toward the SWFP along the streamlines indicated in Fig. 4.11, and horizontal spreading of the patch during travel to the vicinity of the intakes is calculated. Vertical mixing is neglected.

Table 4.4. Dilution Ratios for Samarium Samples Collected at the SWFP

Date	Time CST	C_F, µg/ℓ	Dilution Ratio, $\frac{C_I}{C_F}$
		Crib Samples	
3 Mar.	2220	61.0	4.7×10^3
"	2310	7.7	3.7×10^4
4 Mar.	0030	2.8	1.0×10^5
"	0300	6.7	4.2×10^4
"	0430	102.1	2.8×10^3
"	0450	6.1	4.7×10^4
"	0720	2.4	1.2×10^5
"	1040	5.0	5.7×10^4
"	1200	2.1	1.4×10^5
"	1220	5.1	5.6×10^4
"	1520	1.6	1.8×10^5
		Shore Samples	
3 Mar.	2200	2.9	9.8×10^4
"	2250	1.6	1.8×10^5
"	2340	4.0	7.1×10^4
4 Mar.	0300	1.6	1.8×10^5
"	0450	1.6	1.8×10^5
"	0710	2.7	1.1×10^5
"	1100	1.8	1.6×10^5
"	1200	1.9	1.5×10^5

Note: Initial concentration (C_I) = 0.284 g/ℓ.
C_F = final concentration.

The advection-diffusion equation for these estimates becomes

$$\frac{\partial \phi}{\partial t} + U \frac{\partial \phi}{\partial x} = \frac{\partial}{\partial x}\left(D_H \frac{\partial \phi}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_H \frac{\partial \phi}{\partial y}\right) \quad (1)$$

where ϕ = concentration

U = current speed parallel to the streamlines, assumed uniform in time and space,

t = time

x,y = longitudinal and lateral coordinates, respectively (curvature of the streamlines is neglected), and,

D_H = horizontal or lateral mixing coefficient.

For mixing in the canal, solution to Eq. (1) for an instantaneous source of finite size was found for the case of a constant lateral mixing coefficient (Csanady, 1972). On March 2, 1977, the average transport velocity from the tagging point, in the canal, to a point 2 km into the lake was about 0.085 m/s. The lateral mixing coefficient was estimated to be about 0.01 m^2/s (Fischer, 1973). Computations indicate that in the lake offshore of the canal, about 2 km from the tagging location, the tagged patch has nominal dimensions (four standard deviations of the concentration profile) of about 80 m on a side. The dilution ratio, based on the initial concentration of Sm and the maximum concentration at the center of the patch, was about 127.

Mixing of the tagged effluent as it is transported along the bottom in the lake, from the location offshore of the IHC to the vicinity of the SWFP's intakes, was estimated for the case of a variable horizontal mixing coefficient. Experimental observations of mixing in the Great Lakes (Csanady, 1972, Huang, 1971) and the oceans (Okubo, 1971) have indicated that D_H may not be constant, but rather that it increases as the scale or width of the plume increases. The relationship for these observations takes the form,

$$D_H = k\, S_H^n \quad (2)$$

where S_H = the standard deviation of the concentration distribution, and

k,n = experimental constants.

Values for n vary from 0-1.5 and, for the estimates of mixing made here, n = 1 and 4/3 were used for linear and "4/3's law" mixing, respectively.

For the tagged patch measuring approximately 80 m x 80 m outside the IHC, a mean lake current of 0.13 m/s,* and patch transport of 12 km northwestward to the intakes, the calculation with $n = 1$ and $k = 0.00142$ m/s (Okubo, 1971) yields a patch with a nominal diameter of 530 m in the vicinity of the intakes. The dilution ratio for mixing in the lake, based on the maximum concentration at the center of the patch, is about 24. Together with the dilution due to mixing in the canal, this yields a dilution ratio, based on the initial tagged-water Sm concentration of $(24)(127) \approx 3.0 \times 10^3$.

A similar calculation, employing $n = 4/3$ and $k = 0.000463$ $m^{2/3}/s$, indicates a patch with a nominal diameter of 770 m in the vicinity of the intakes with a dilution ratio for mixing in the lake of about 48. Thus, the dilution ratio based on the initial tagged water Sm concentration is $(48)(127) \approx 6.1 \times 10^3$.

The dilution ratios calculated are for the center of the patch and are thus minimum values for the tagged effluent. The exact location of the patch relative to the intakes is not known as no measurements of the tagged water mass were made in the intake area. However, the dilution ratios calculated for the center of the patch are of about the order of magnitude of and smaller than those determined from sampling at the crib and shore intakes (Table 4.4). The travel time from the tagging location to the intakes, based on the mean currents used in the mixing estimates, was about 32 hr. (Sm was detected in the intake waters about 33 hr after tagging.)

The results of these comparisons should be viewed with some caution. Models with alternate mixing laws and assumptions about the trajectory of the patch might give reasonable results as well. The small amount of tagged IHC water may not have moved as a single discrete patch toward the intakes but rather in several patches due to interruption by the Calumet Harbor

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*In an earlier report on these estimates (Harrison, McCown, Raphaelian, and Saunders, 1977) a mean speed of 0.08 m/s (based on time-averaged current-meter records) was used. Subsequent analysis of the current-meter records for the specific period of the experiment indicated that lake currents as large as 0.13 m/s were measured. Speeds of this magnitude are consistent with those estimated from time-of-travel data for the tracer, and are used in this report. Minor, and insignificant, differences in dilution estimates result from this change that was made to provide consistent tracer time-of-travel values.

Breakwater. What can be stated is that the application to the tracer experiment of a turbulent diffusion model yielded dilution results which were not vastly different from dilutions inferred from measurements.

4.2.3.3 Dilution Estimates for the Entire IHC Effluent

The estimates, given above, of dilution of the tagged portion of the IHC effluent, while not verified, do not contradict the values inferred from experimental data. They suggest that the application of a turbulent mixing model together with the inferred advection field may be an appropriate representation of the behavior of an IHC sinking plume. It is instructive to apply a similar model to estimate the dilution of the *entire* IHC effluent sinking plume as it was transported toward the SWFP's intakes under the conditions that prevailed during the tracer experiment.

For the case of a sinking plume formed by the entire IHC effluent, the plume is considered to be a steady, continuous source of some conservative tracer emanating from the mouth of the IHC and to be transported northwestward by the flow field given in Fig. 4.12. In this case, vertical mixing is again neglected and, now, horizontal mixing is considered important only in the lateral (normal to streamline) direction. Eq. 1 reduces to the form

$$U \frac{\partial \phi}{\partial x} = \frac{\partial}{\partial y} \left(D_y \frac{\partial \phi}{\partial y} \right), \tag{3}$$

where D_y = lateral (y) mixing coefficient
and is given by

$$D_y = k S_y^n . \tag{4}$$

The centerline of the plume (x coordinate) was assumed to follow the streamline in Fig. 4.11 that is nearest to shore and was assumed to begin (x = 0) on that streamline in the lake opposite the IHC entrance with an initial width of 300 m, approximately the width of the IHC entrance. Solutions to Eqs. (3) and (4) were found (Brooks, 1960) as a function of distance along the plume for mean current of 0.13 m/s, n = 4/3, and k = 0.000463 $m^{2/3}/s$. The effects of the shoreline, as a reflective boundary, have been included but are minor.

At 12 km, in the vicinity of the shore and crib intakes, the centerline (minimum) dilution-ratio is about 2.8. If it is assumed that the plume

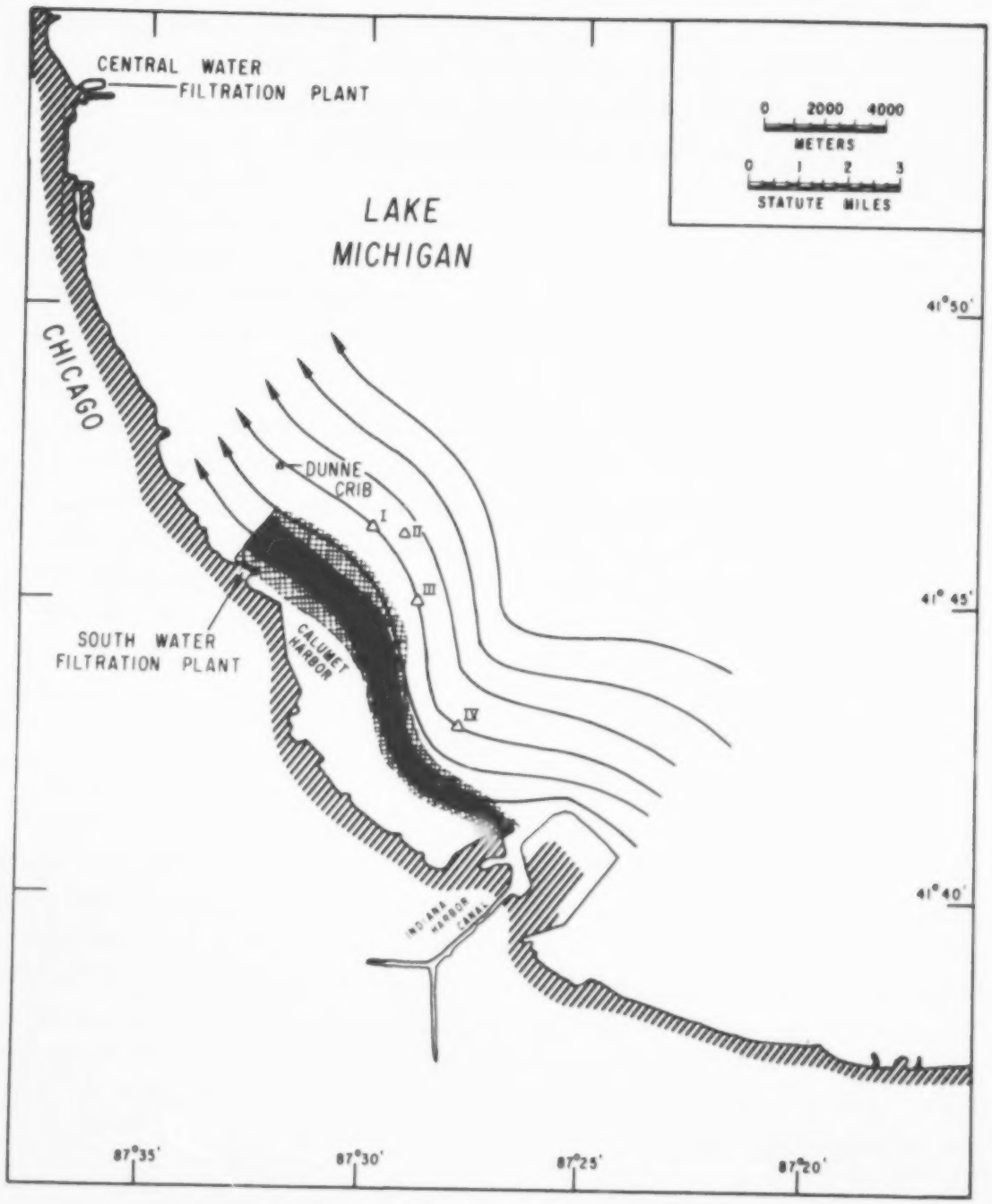

Fig. 4.12. Schematic Representation of the Expected Dilution Ratios in the Nearshore Waters of Southwestern Lake Michigan on March 3, 1977. (The cross hatching represents dilution ratios in the range 10-100; solid black represents dilution ratios in the range 1-10)

centerline coincides with the streamline nearest shore in Fig. 4.11, the dilution ratio at the shore intake is about 1.3×10^2 and at the crib is greater than 10^5. Figure 4.12 depicts the contours of dilution ratios of 10 and 100 determined in the calculations for the conditions stated above. These results provide only an approximate description of the mixing of the IHC plume under a specific set of inferred currents and plume trajectory. Although this type of estimate may have some validity for the case studied, the effects of vertical mixing, of the unsteady nature of the currents, of interactions with harbor structures, and of transport along other streamlines could act either to increase or decrease dilution ratios at the crib or shore intake.

Finally, the information gathered on the current structure can be used to estimate a bound on the average dilution ratio that may be expected should the entire IHC effluent mix uniformly with the nearshore lake waters. The volume flux out of the IHC during the study was about 120 m^3/s. The average speed of the lake water in the vicinity of the canal was about 0.08 m/s. If we assume that all of the water within 4 km of shore mixes with the IHC effluent, for an average depth of 10 m, a volume flux of about 3200 m^3/s of lake water mixes with the IHC effluent. This results in an average dilution ratio of about 27.

In summary, for the set of environmental conditions studied, it appears that uniform mixing of the entire IHC effluent with nearshore lake waters produces an average dilution of 27 at the intakes. In the more likely event that the IHC effluent moves northwestward as a plume, the minimum dilution ratio estimate on the plume centerline is about 2.8. Larger dilution ratios are found at the shore and crib intakes, if the plume centerline does not cross them. The values of those dilution ratios depend on the particular trajectory of the plume relative to the intakes. For the conditions assumed above, dilution ratios of about 1.3×10^2, and $>10^5$, were estimated for the shore and crib intakes, respectively.

Clearly, verification of even the simple estimates of mixing proposed for the tagged portion of the IHC effluent and the entire IHC effluent requires more detailed flow field data and tracer measurements in the tagged patch. However, the transport of the Sm tracer from the IHC to the SWFP's intakes provides unequivocal evidence that the sinking plume from the IHC

reaches the intakes, and dilution estimates suggest the possibility of rather limited dilution of the IHC effluent by the time it reaches the intakes for some transport paths.

4.3 COMPARISON OF THE POTENTIAL FOR POLLUTANTS FROM FLOATING AND SINKING PLUMES OF THE IHC TO ENTER THE CITY OF CHICAGO'S RAW WATER INTAKES AT THE SWFP

Historically, water quality data from Chicago's SWFP have shown that major pollution episodes occur almost exclusively in the winter when the IHC plume is sinking. That these episodes do not occur in summer would be explained if lake stratification prevented pollutants from crossing the thermocline to reach the depth of the crib intake. However, the fact that the lake is stratified during the summer (floating plume) is not sufficient to explain why pollution episodes do not occur in the summer because the thermocline is rarely above the 9.1-m (30-ft) depth of the Dunne Crib's intake on the lake bottom. The average intake water temperature at the Dunne Crib during June-October is ≈16-21°C (60-70°F) (M. Kniahynycky, per. comm., 1978) but water below the thermocline is ≈4°C (40°F). In addition, water temperature data collected off the Chicago coast in the summer of 1976 (Harrison, W., et al, 1977) indicate that the thermocline was below 22 m (72 ft) much of the period from July through mid-October, 1976.

The most significant difference between winter sinking-plume conditions and summer floating-plume conditions, in terms of severe pollution events, is that the sinking-plume carries IHC water along the bottom directly to the Dunne Crib intake which is also near the bottom. Although vertical diffusion acts to mix IHC water upward in the winter and downward, from the surface, in the summer, that mixing is apparently not significant enough to mitigate the intake of sinking-plume waters in the winter nor to result in the intake of large amounts of floating-plume waters in the summer.

Another contributing factor is that the core of ≈4°C water that forms after sinking at the IHC mouth during a period of northwestward flowing lake currents, may be horizontally constrained. As discussed in Sec. 4.2.3.1, the IHC entrance and the Dunne Crib's intake are both at 9.1 m (30 ft) depth. IHC water which has sunk to the bottom may be constrained in horizontal mixing by the "uphill" bottom slope on the shoreward side. In contrast, the floating plume at the surface is horizontally constrained only by the shoreline.

The final factor investigated was the existence, in winter, of currents of longer and/or stronger duration than in the summer. Unfortunately, there are little current data available, thus, no conclusive evidence exists. In reviewing the current data that are available, one instance (mid-July, 1976) was found when the currents would have been sufficient to move IHC water from the IHC to the SWFP intakes. There was no odor problem at the SWFP during this period (Phil Reed, personal communication, 1978). One instance, however, is certainly not conclusive.

Of the mechanisms discussed above, the two significant factors, intense downward forces at the subduction zone and horizontal mixing constraints, combine to allow the transport of considerably less diluted IHC water northward to the SWFP's raw water intakes during the winter when the IHC plume is sinking than during the summer when the plume is floating.

5 SUMMARY

The purpose of the program discussed in this report was:

1. To develop methods for simultaneously tagging both oily wastes and the underlying waters, each with a unique tracer, and for determining their individual motions in fresh coastal waters, and
2. To apply these methods to specific, contaminated coastal waters.

The method developed to trace the oily wastes involved using the rare earth element (REE) dysprosium (Dy) to tag the oily waste. Dy was chosen because it could be detected in very low concentrations by neutron activation analysis (NAA). Numerous bench tests were performed to test the retention of Dy by the oily-waste as discussed in Sec. 2.1.2.2. Dy seems to be a good tag for oily-wastes with only a maximum of 0.4% Dy migration into the underlying waters during the bench tests and probably even smaller percentages during field experiments.

A second REE samarium (Sm) was chosen to tag the water under the oily waste. Sm was chosen because it's NAA characteristics are similar to Dy, although it cannot be detected in concentrations as low as Dy. The Sm was chelated with DTPA (Sec. 2.1.2.1) to increase its persistence in the water.

A rapid NAA method was developed in this program for the detection of Dy and Sm. The method required no sample preparation other than evaporation of the liquid and cleaning of the Polyvial. The sample size required was only 15 mL for detection in the ng/L range; approximately 17 samples an hour could be analyzed; and each sample was analyzed simultaneously for both Dy and Sm.

Finally, the unique tracer technique was applied to the Indiana Harbor Canal (IHC) to trace both the oily-waste poured on the canal surface and the underlying canal effluent. Two experiments in the IHC and adjacent waters of Lake Michigan were carried out. They occurred in the summer when the canal water floats on the surface of Lake Michigan (Sec. 3) and in the winter when the canal water sinks to the lake bottom (Sec. 4).

The summer floating-plume experiment indicated that:

1. When the tagged oil was subjected to severe downward mixing by a passing ore carrier, it did not resurface but remained mixed in the water column (Sec. 3.1.7),

2. Lake diffusion coefficients calculated from the Dy and Sm data were similar to diffusion coefficients determined by others in the Great Lakes (Sec. 3.1.5) using other tracer techniques, and

3. After the oil was mixed into the water column by the ore carrier there were no distinquishable differences between the movement and diffusion of the oil/Dy and the movement of the water/Sm (Sec. 3.2.3).

The winter sinking-plume experiment indicated that:

1. Unequivocal evidence of the transport of IHC effluent to the raw water intakes of the City of Chicago's South Water Filtration Plant (SWFP) was provided by means of the tracer (Sec. 4.1.3),

2. A partitioning of the oily wastes and underlying water was made apparent by the employment of the unique dual tracer system (Sec. 4.2.4.1), and

3. Simple model estimates of IHC plume dilution at the SWFP were supported by the experimental measurements and these estimates showed centerline dilution ratios may be as low as 2.8 (Sec. 4.3.3.2).

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APPENDIX A

Plan-View Contoured Plots of Dy and Sm Concentrations,
Floating Plume (Refer to Fig. 3.1 for position of cloud)

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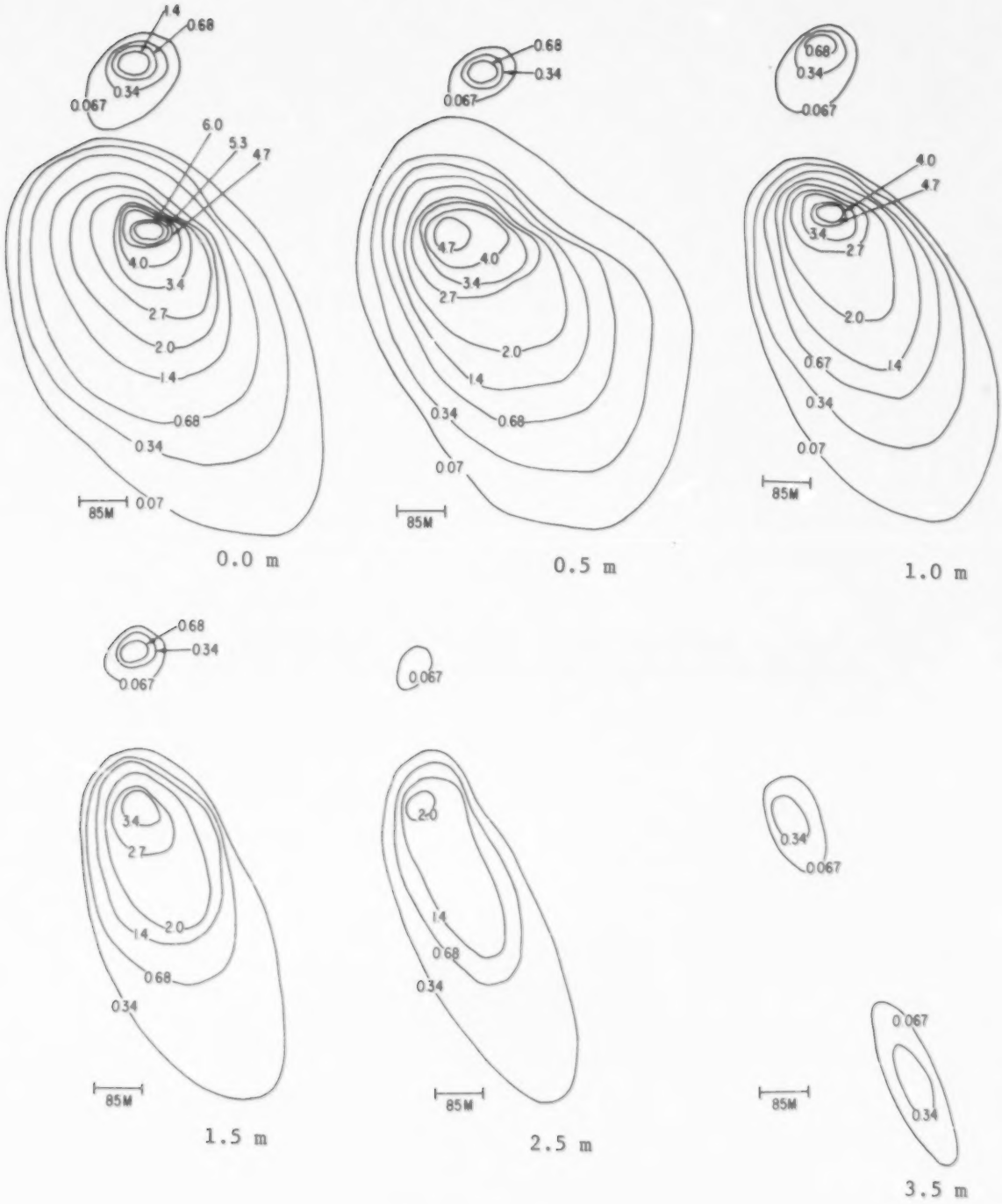

Fig. A1. Plan-View Contoured Plot of Dy Concentrations (μg/l) at 0.0, 0.5, 1.0, 1.5, 2.5, 3.5-m Depths for Floating-Plume #1

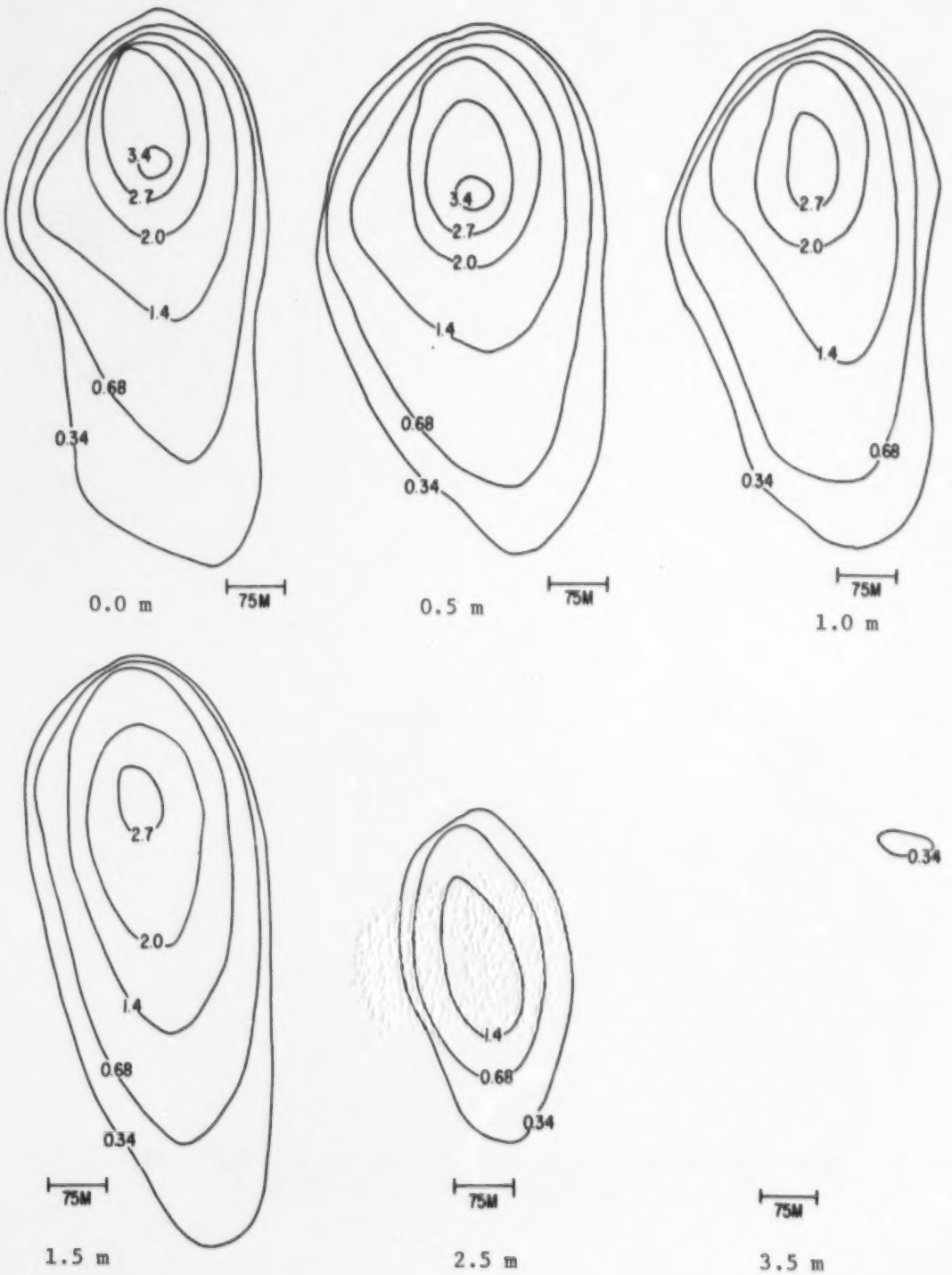

Fig. A2. Plan-View Contoured Plot of Dy Concentrations (µg/l) at 0.0, 0.5, 1.0, 1.5, 2.5, 3.5-m Depths for Floating-Plume #2

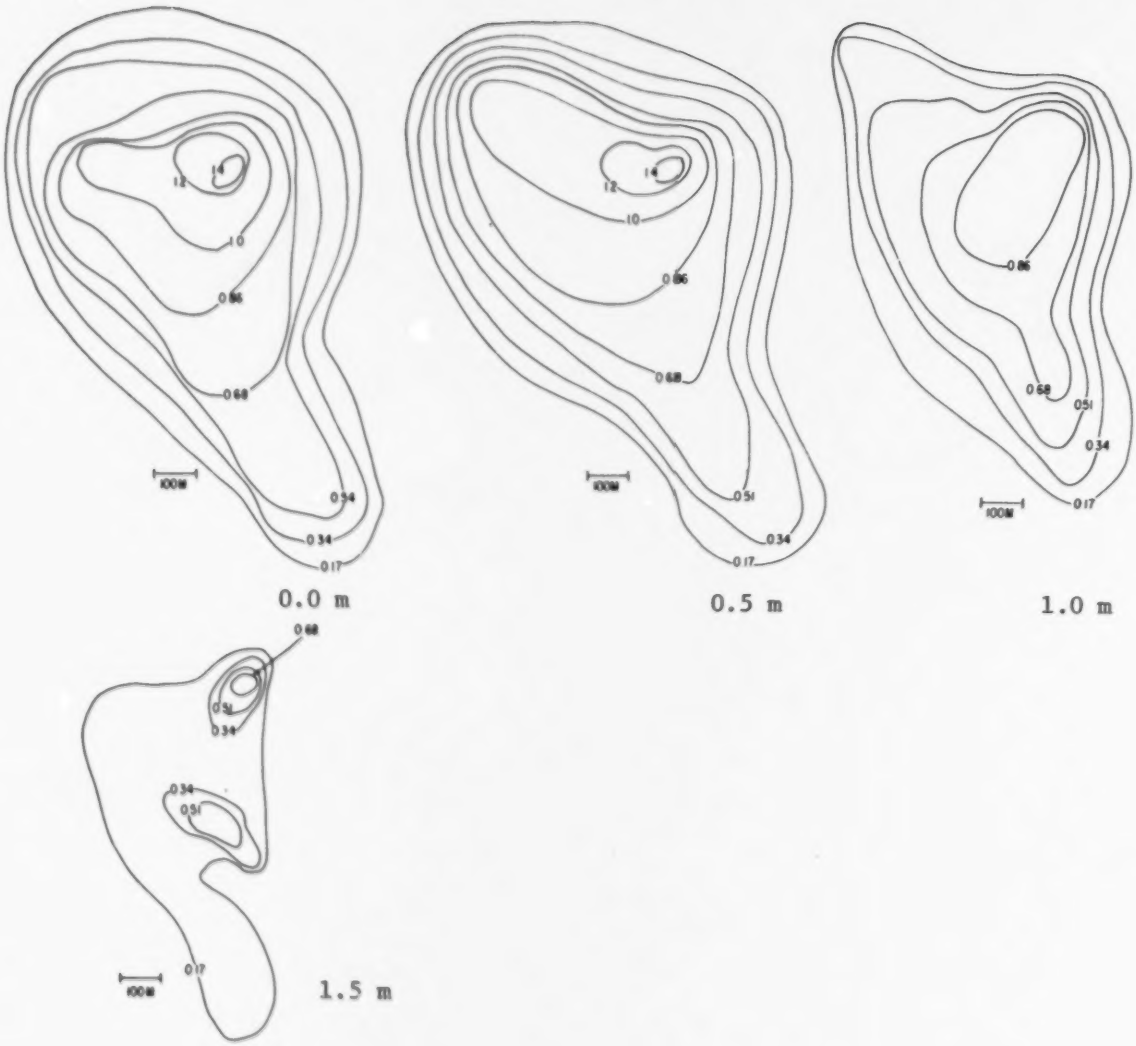

Fig. A3. Plan-View Contoured Plot of Dy Concentrations (μg/L) at 0.0, 0.5, 1.0, 1.5, 2.5, 3.5-m Depths for Floating-Plume #3

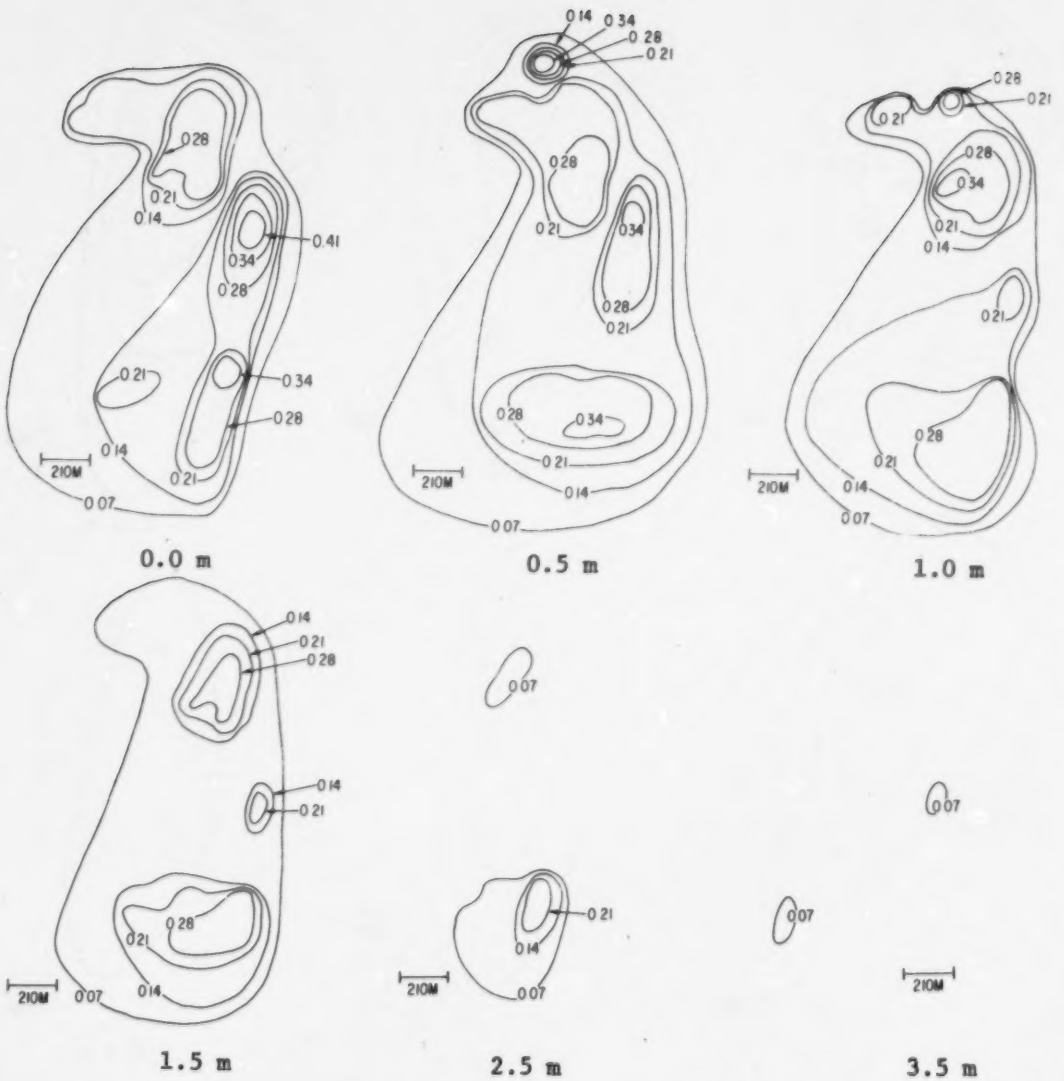

Fig. A4. Plan-View Contoured Plot of Dy Concentrations (µg/L) at 0.0, 0.5, 1.0, 1.5, 2.5, 3.5-m Depths for Floating-Plume #4

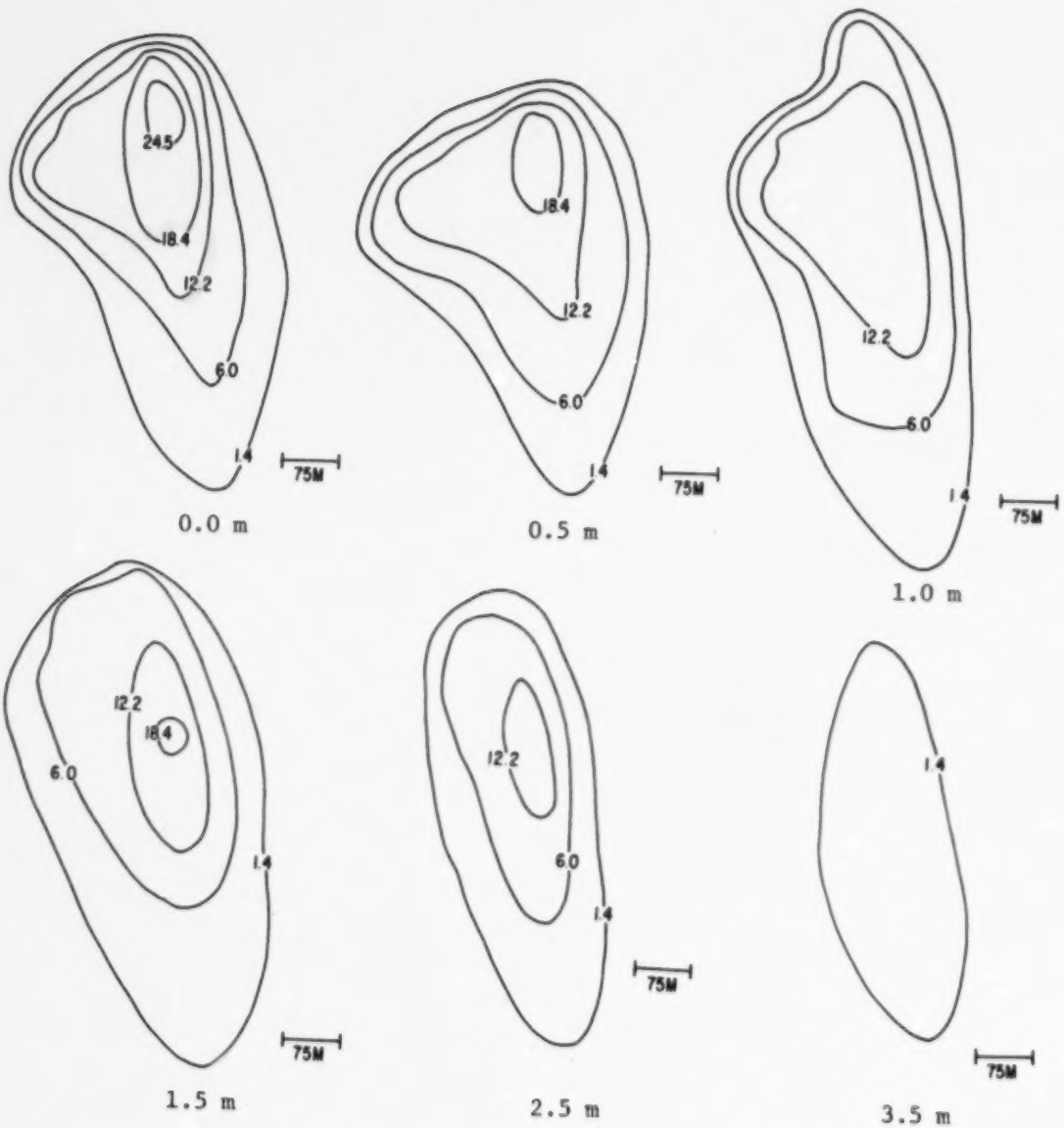

Fig. A5. Plan-View Contoured Plot of Sm Concentrations (μg/L) at 0.0, 0.5, 1.0, 1.5, 2.5, 3.5-m Depths for Floating-Plume #2

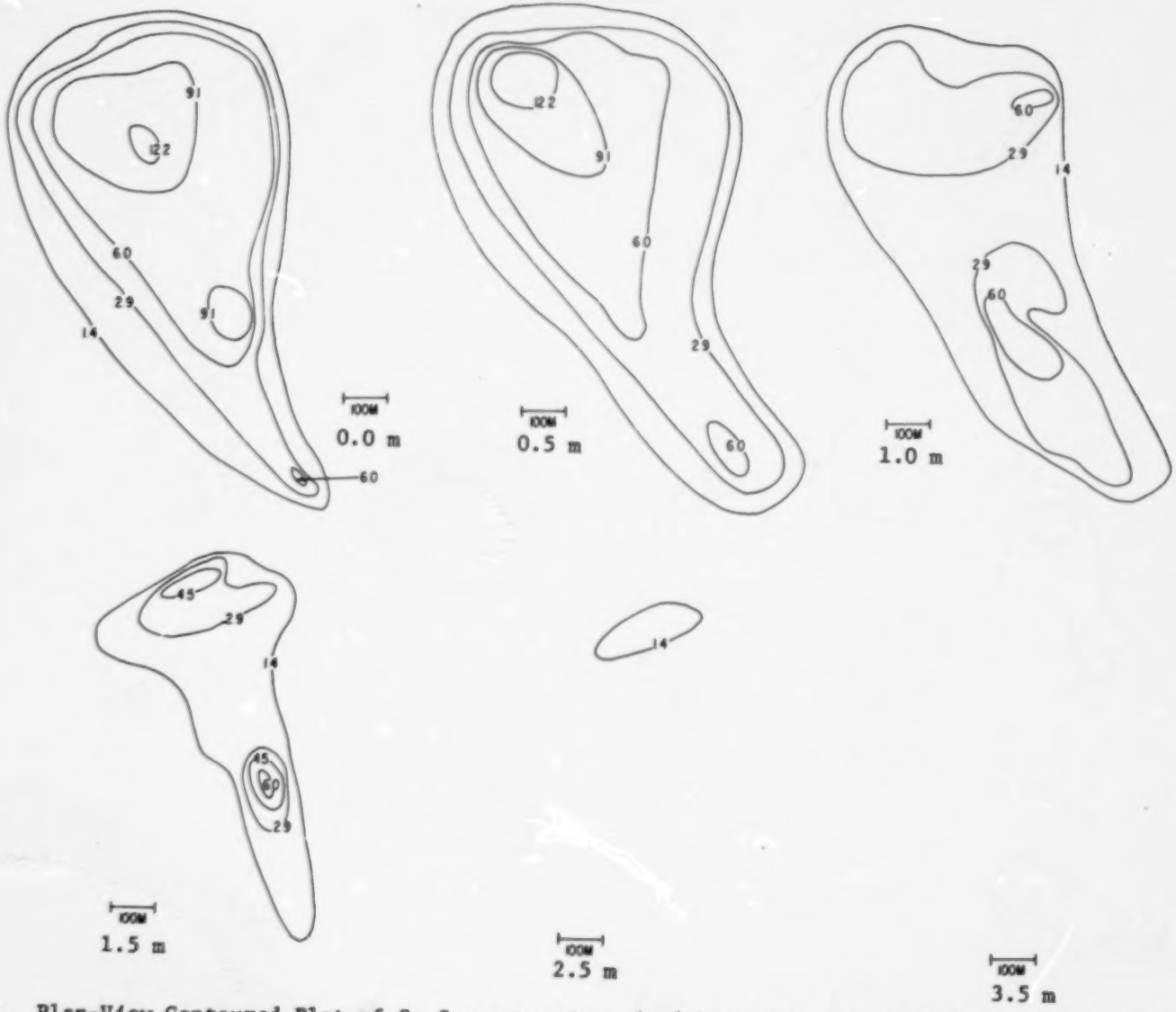

Fig. A6. Plan-View Contoured Plot of Sm Concentrations (µg/L) at 0.0, 0.5, 1.0, 1.5, 2.5, 3.5-m Depths for Floating-Plume #3

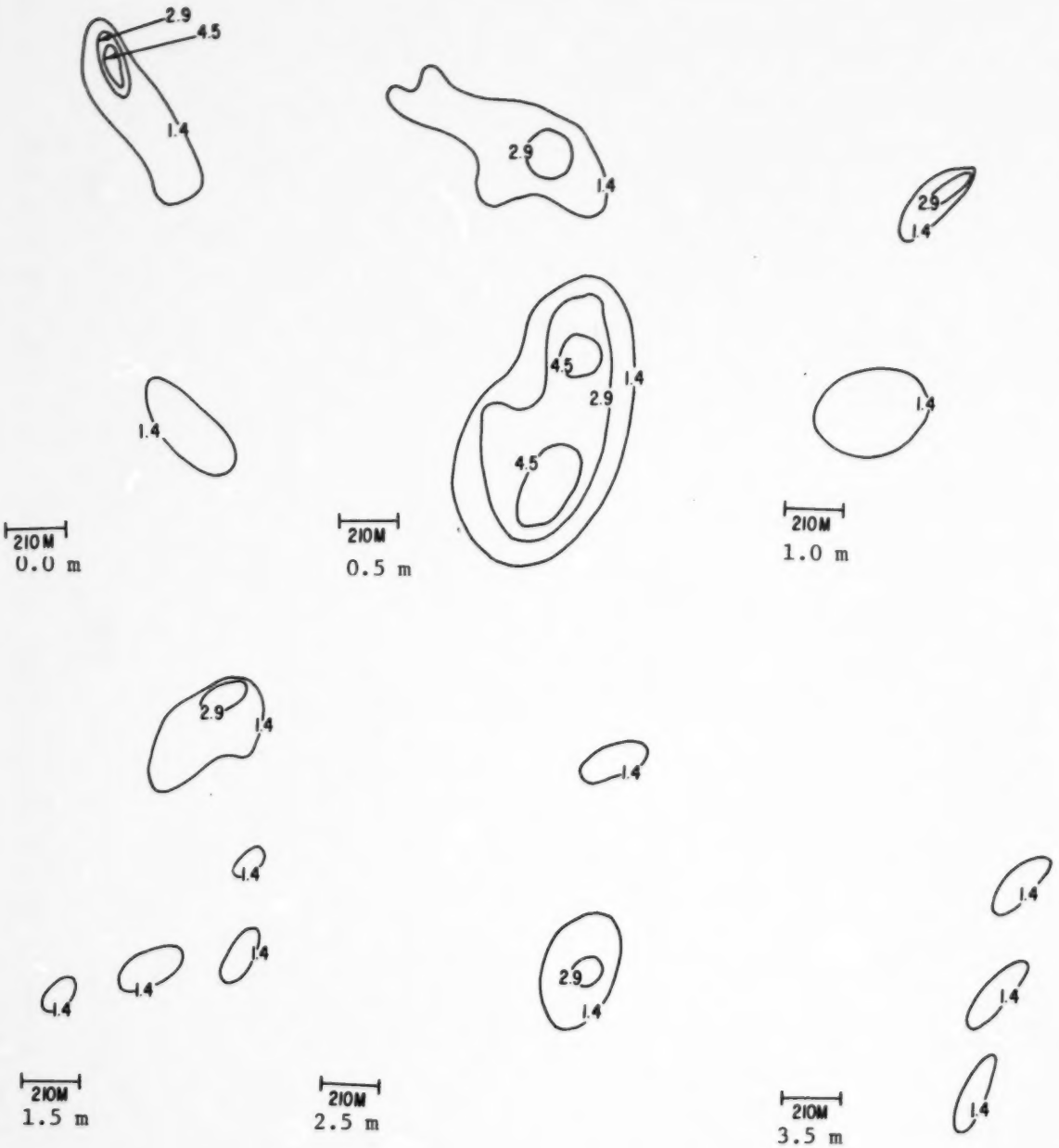

Fig. A7. Plan-View Contoured Plot of Sm Concentrations (μg/L) at 0.0, 0.5, 1.0, 1.5, 2.5, 3.5-m Depths for Floating-Plume #4

APPENDIX B

Vertical Section Plots of Dy and Sm Concentrations
and Near Bottom Dye Concentrations, Sinking Plume
(Refer to Fig. 3.5 for Position of Transects)

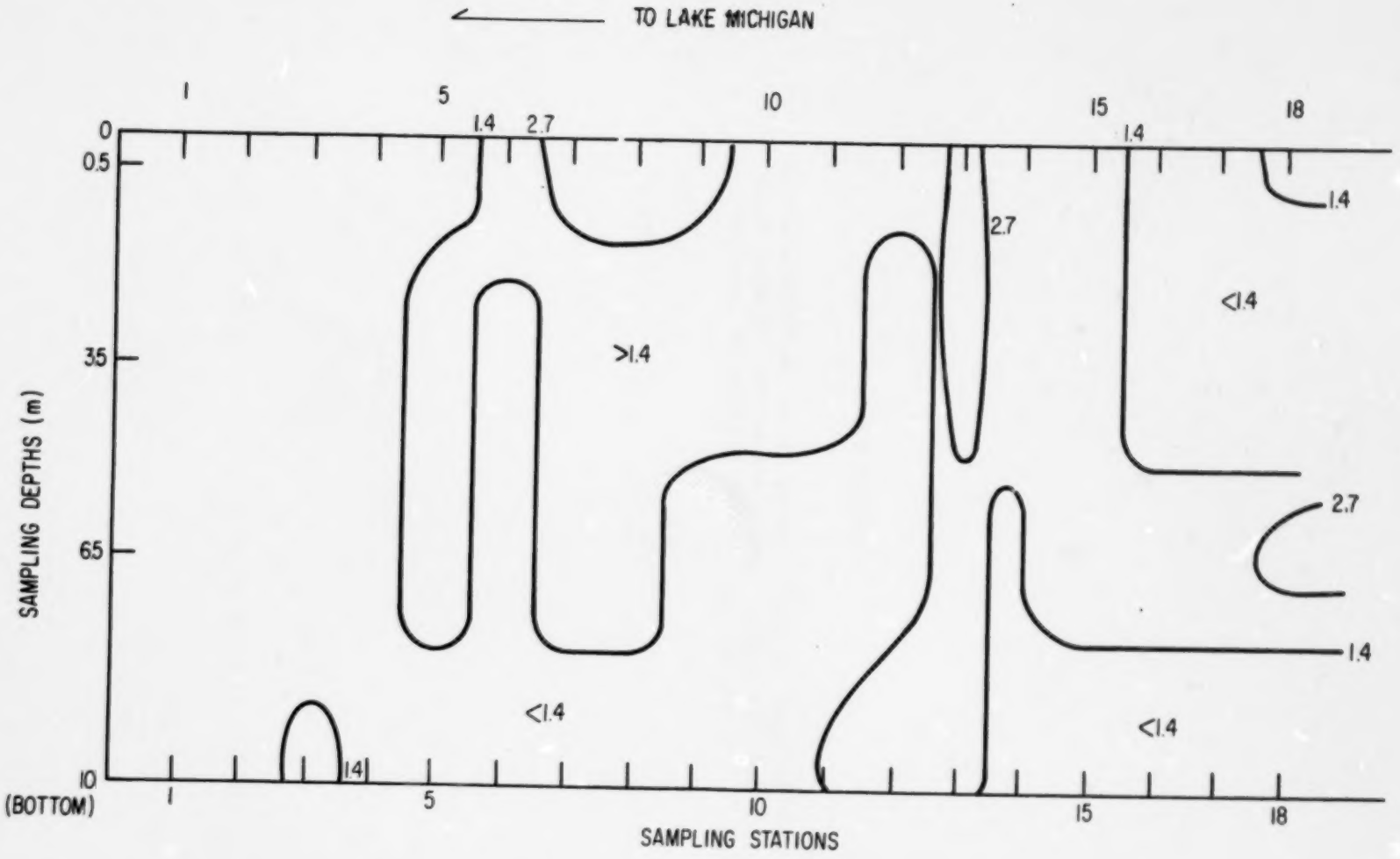

Fig. B1. Transect A: Sm Concentrations. (Concentrations in µg/L. All 90 Samples Collected Were Analyzed.)

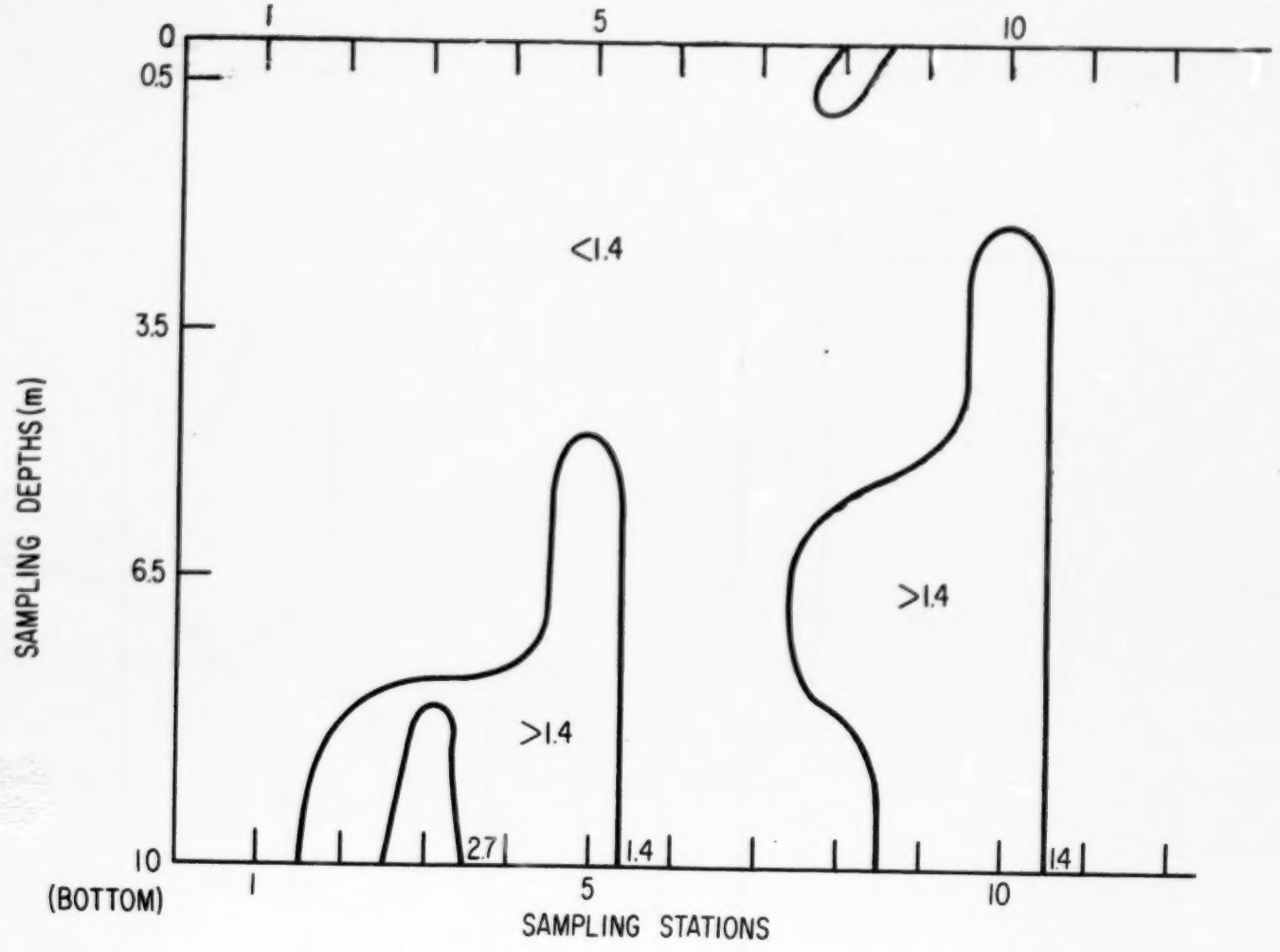

Fig. B2. Transect B: Sm Concentrations. (Concentrations in µg/L. All 55 Samples Collected Were Analyzed.)

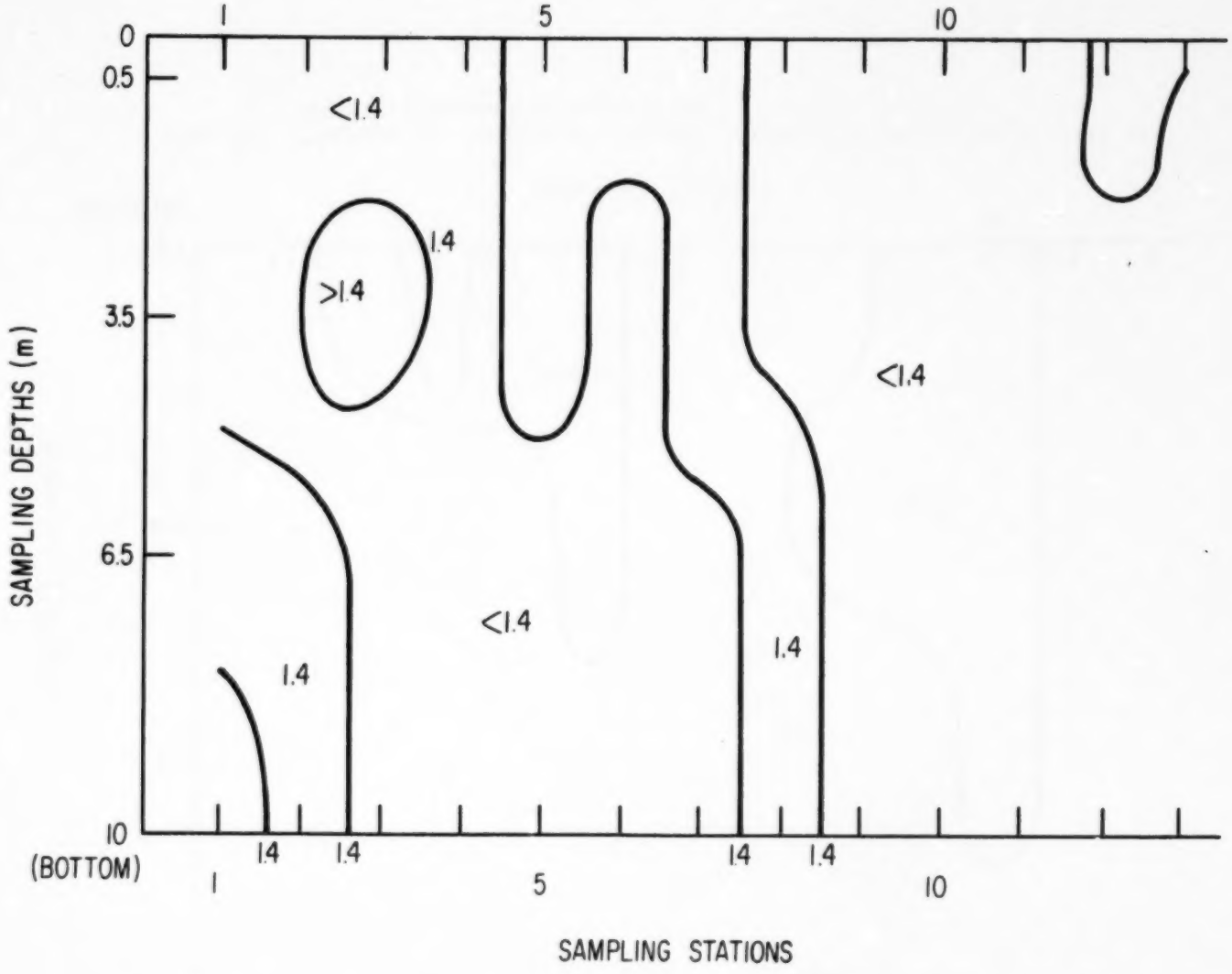

Fig. B3. Transect C: Sm Concentrations. (Concentrations in µg/L. All 65 Samples Collected Were Analyzed.)

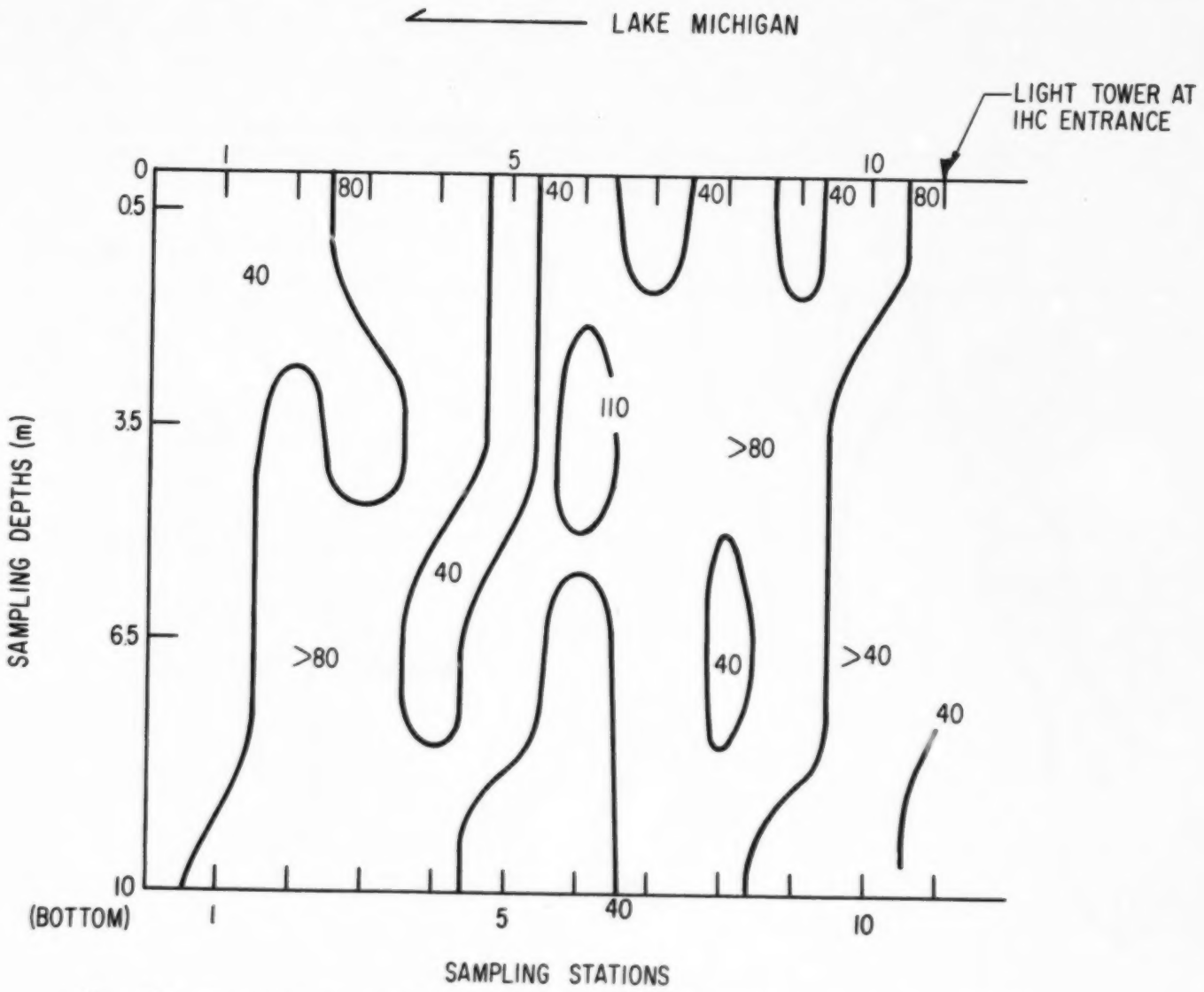

Fig. B4. Transect B: Dy Concentrations. (Concentrations in ng/L. All 55 Samples Collected Were Analyzed.)

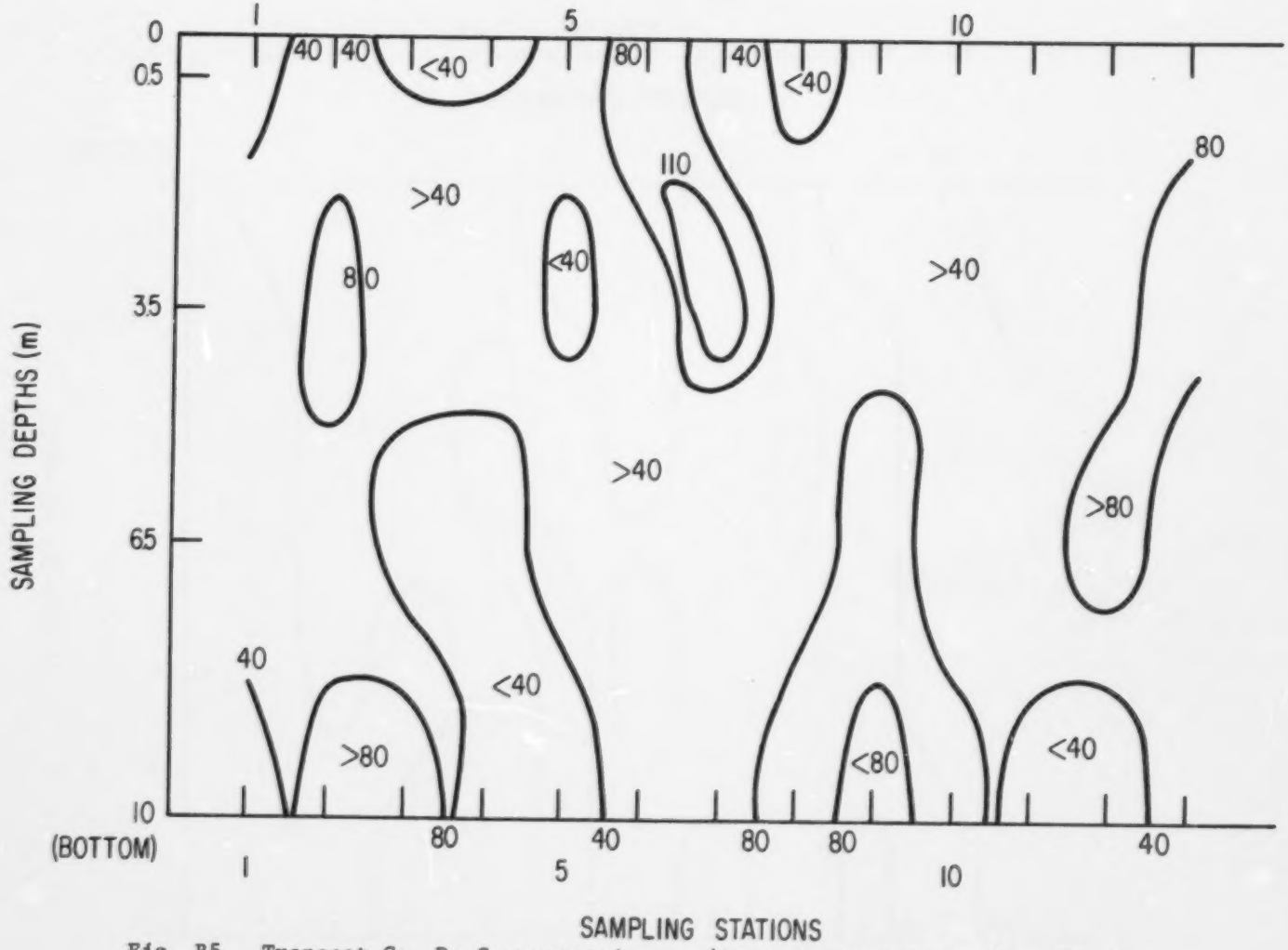

Fig. B5. Transect C: Dy Concentrations. (Concentrations in ng/L. All 65 Samples Collected Were Anlyzed.)

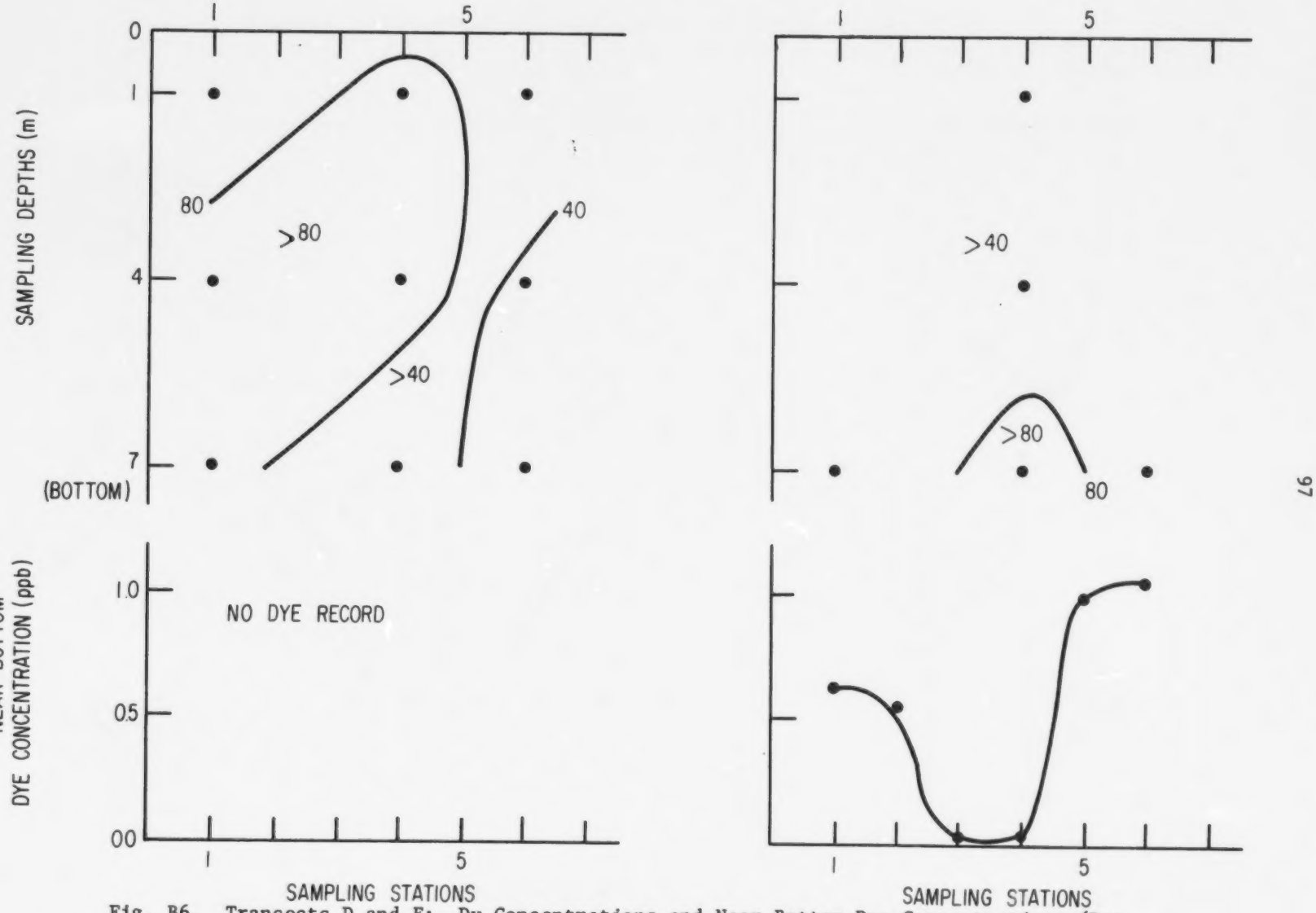

Fig. B6. Transects D and E: Dy Concentrations and Near Bottom Dye Concentrations (Dot Indicates Sample Analyzed at that Point, Dy Concentrations in ng/L)

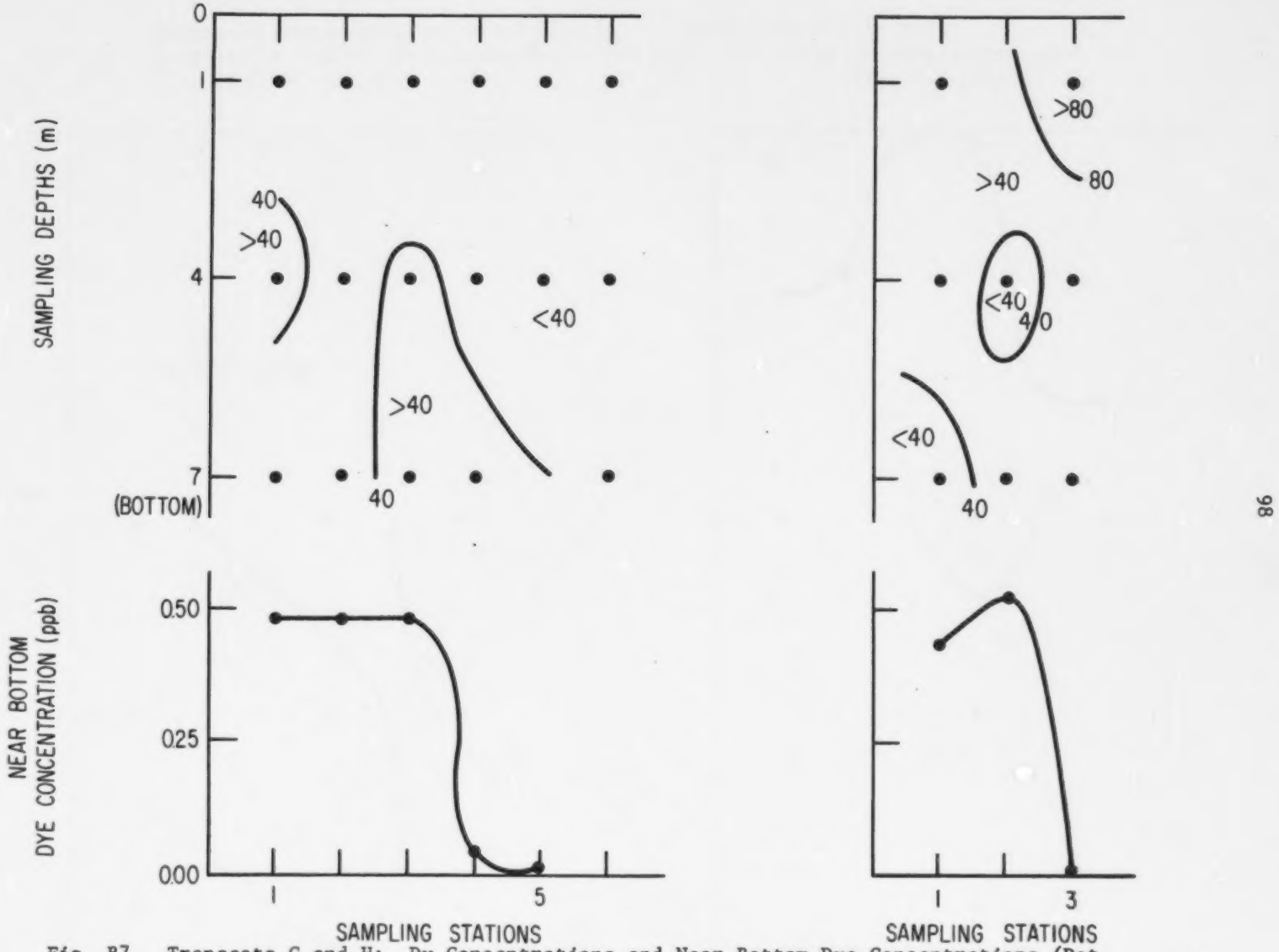

Fig. B7. Transects G and H: Dy Concentrations and Near Bottom Dye Concentrations (Dot Indicate Sample Analyzed at that Point, Dy Concentrations in ng/L)

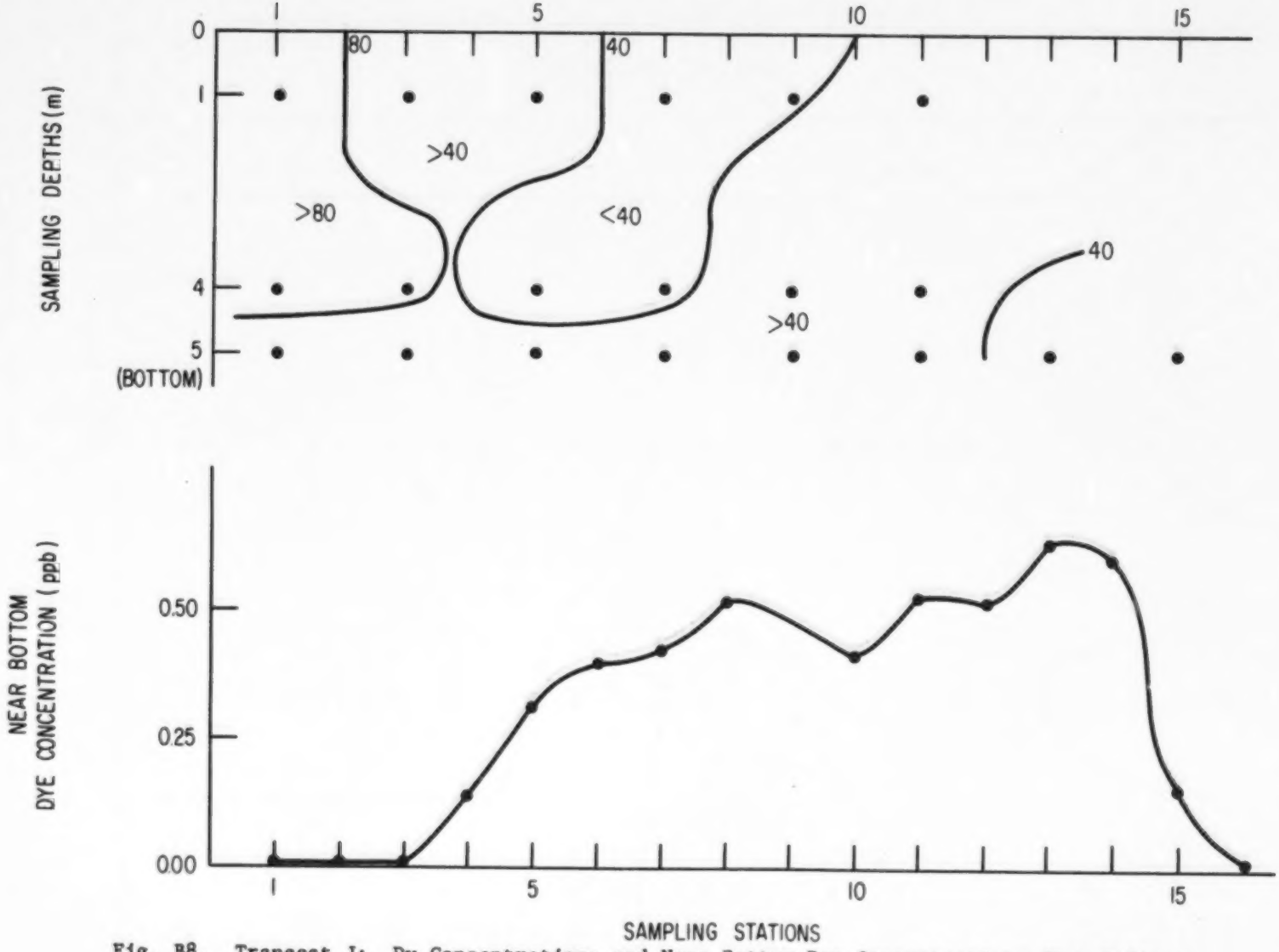

Fig. B8. Transect J: Dy Concentrations and Near Bottom Dye Concentrations (Dot Indicate Sample Analyzed at that Point, Dy Concentrations in ng/L)

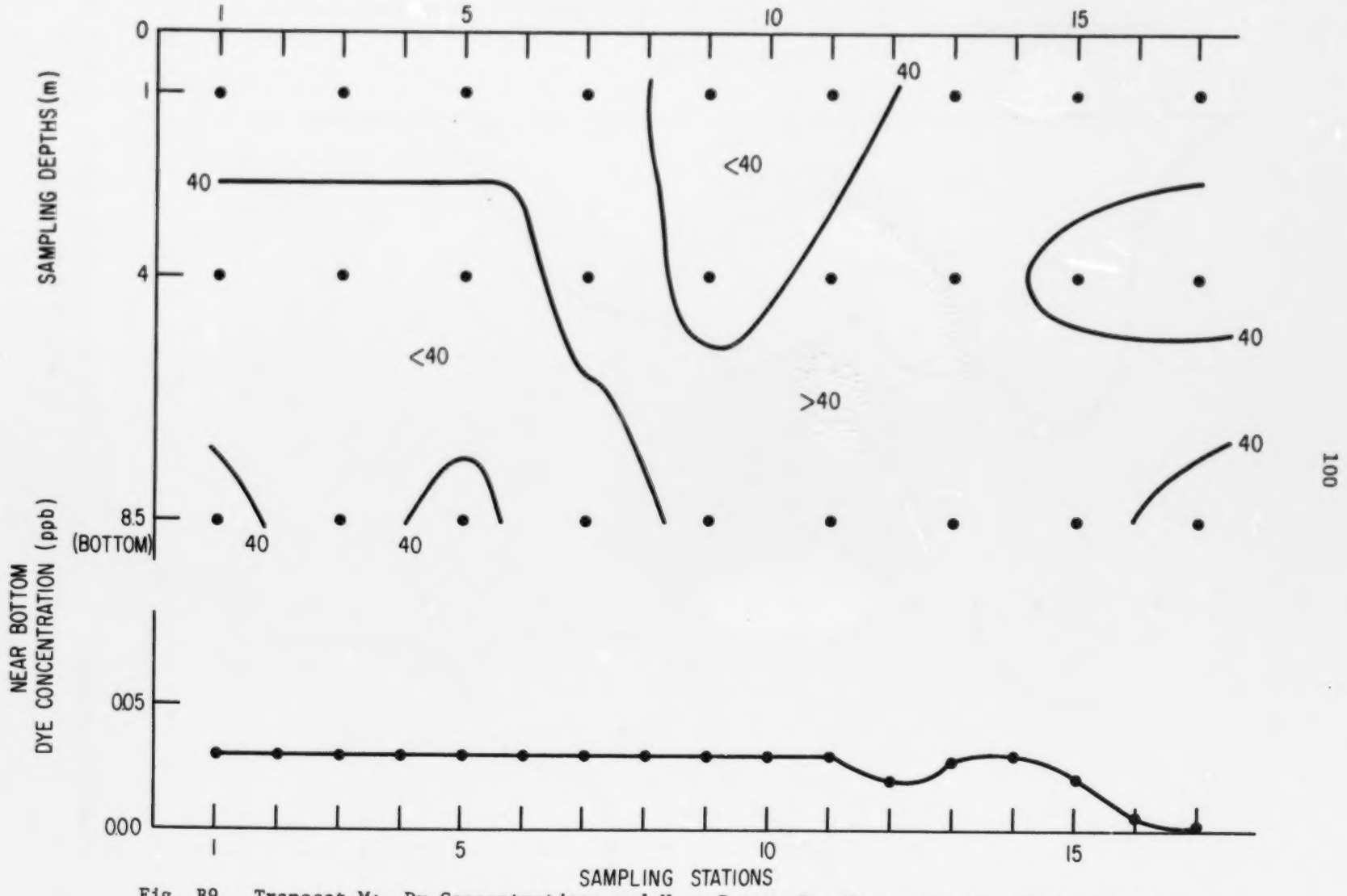

Fig. B9. Transect M: Dy Concentrations and Near Bottom Dye Concentrations (Dot Indicate Sample Analyzed at that Point, Dy Concentrations in ng/L)

Fig. B10. Transect O: Dy Concentrations and Near Bottom Dye Concentrations (Dot Indicate Sample Analyzed at that Point, Dy Concentrations in ng/L)

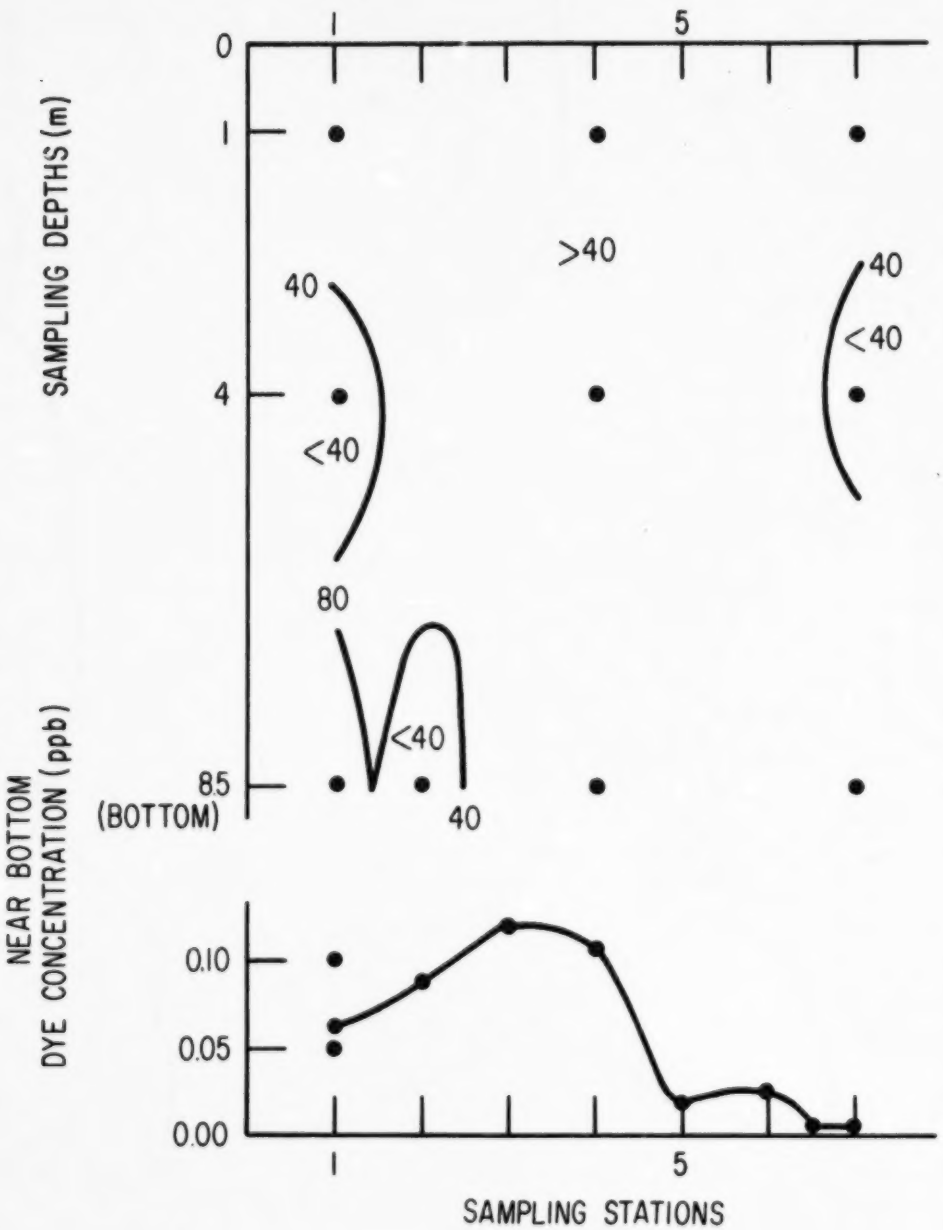

Fig. B11. Transect P: Dy Concentrations and Near Bottom Dye Concentrations (Dot Indicate Sample Analyzed at that Point, Dy Concentrations in ng/L)

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